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## **FERROCENE AND FERROCENE DERIVATIVES**

by

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### **ABSTRACT**

This is an annotated bibliography covering ferrocene and its derivatives from 1962 to August 1966. Several review articles are listed which describe the unique characteristics of ferrocene since its discovery in 1951, its reactions, and some of its uses. Approximately 550 citations are listed.

## FOREWORD

This bibliography of ferrocene and ferrocene derivatives was compiled in response to a request from the Propulsion Laboratory, Research and Development Directorate, U. S. Army Missile Command. The survey was undertaken to provide a comprehensive listing of ferrocene chemistry literature throughout the world from 1962 to August 1966. The 1962 starting date was selected since the literature from ferrocene's discovery in 1951 has been well covered in a number of review articles, through 1961, many of which are included in Section VII.

The principle sources searched were chemical abstracts, and documents of Redstone Scientific Information Center; however, many other journals and abstracting services, both foreign and domestic, were searched for contributing articles. Additional information concerning specific uses of ferrocene and ferrocene derivatives was obtained from Mr. Hans W. Sitarz, Manager, Army Programs, Thiokol Chemical Corporation, Huntsville Division, and from Rohm and Haas Company, Huntsville Division.

Clarification of abbreviations and symbols used in this survey may be found in chemical abstracts.

Dr. Charles U. Pittman, Jr. (First Lieutenant, U. S. Army) would like to thank the Propulsion Laboratory of the U. S. Army Missile Command for the time allotted for this work, and for other active support. In this regard, he would particularly like to thank Messers N. C. White and C. W. Huskins.

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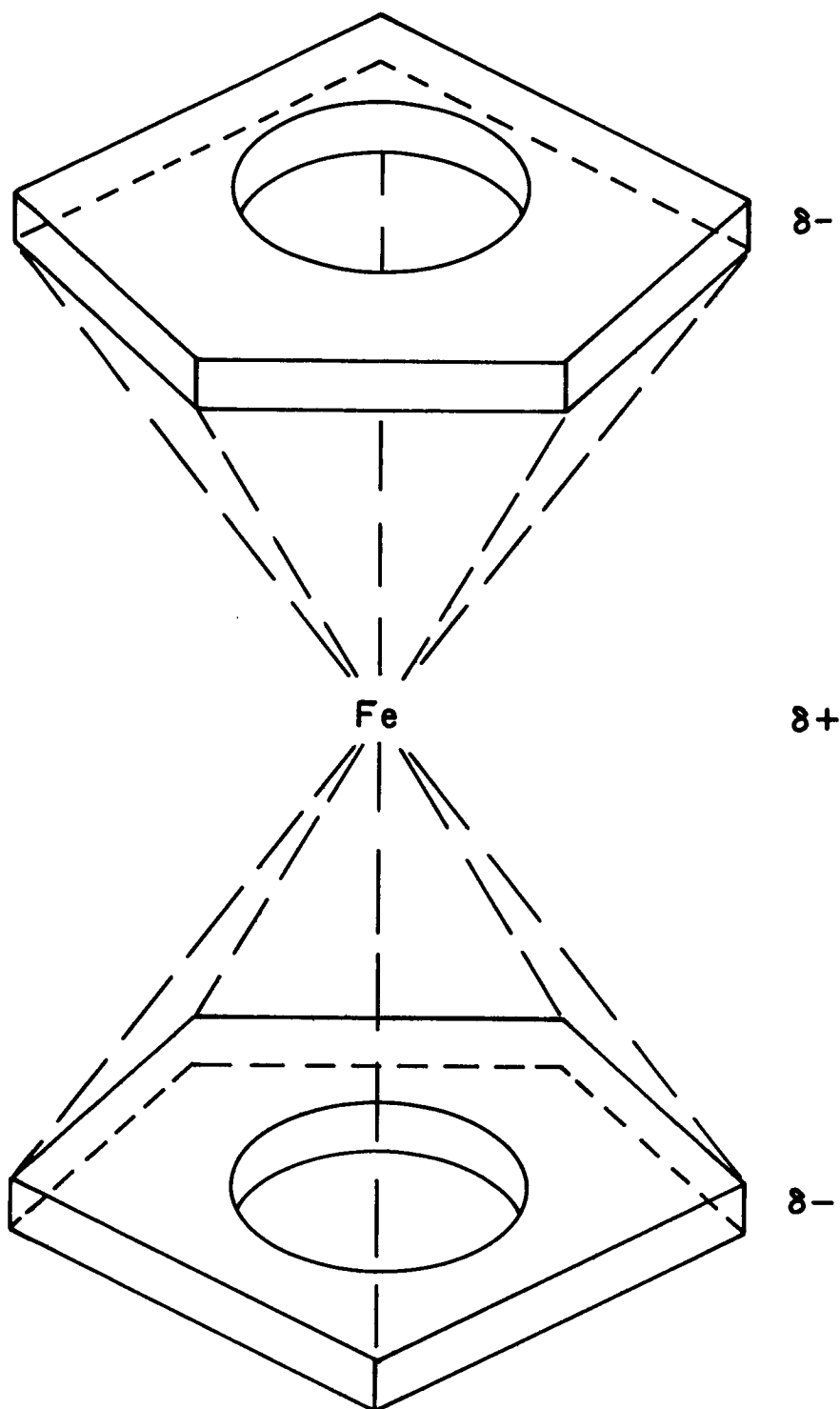
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## INTRODUCTION

In 1951 Kealy and Pauson at Sheffield University discovered dicyclopentadienyl iron, now commonly called ferrocene. This compound possessed properties strikingly different from those of known organometallic compounds, and this attracted the attention of chemists at large. Within a year Woodward, Rosenblum, Whiting, and Wilkinson<sup>2,3</sup> had recognized the unique sandwich structure of ferrocene. The striking aromaticity of the cyclopentadienyl rings was demonstrated by Woodward, Rosenblum, and Whiting. The discovery of ferrocene stimulated intensive research in the cyclopentadiene chemistry of other elements, and in a short 10 years cyclopentadienyl compounds of nearly all the elements of the periodic table had been prepared.

Compounds which have a  $\pi$  bonded sandwich structure are called metallocenes. The research on metallocenes has contributed extensively to an improved understanding of the bonding of transition metals to carbon. Briefly, the structure of ferrocene is that of two planar cyclopentadiene rings which are parallel to each other and have an iron atom sandwiched between them. The two rings are free to rotate about an axis perpendicular to the plane of the rings and equidistant from each of the carbons of the rings. All the carbon-carbon bond distances in the cyclopentadienyl ring are equal, and all carbon-carbon bonds have the same bond order. In this respect the cyclopentadienyl rings resemble the cyclopentadienide anion. The rings are electron rich and have aromatic characteristics. Ferrocene may best be represented as shown in the figure with some net donation of electron density from iron to the rings. Each carbon is symmetrically bonded to the iron.

Ferrocene's unique structure imparts certain characteristic properties to this molecule. The rings, with their aromatic character, undergo many of the reactions of benzene - the most important of which is electrophilic substitution. The ferrocene molecule is easily oxidized to the ferricinium ion.<sup>4</sup> The oxidation can be pictured as the removal of an electron from the iron atom thus raising it to a pseudo-plus-three oxidation state. The unusual thermal stability of ferrocene has stimulated research for ferrocene-based, heat-resistant materials. Its symmetrical structure gives it a high vapor pressure and it is readily sublimed. The ferrocenyl group is a strong electron donating group<sup>5</sup> and it greatly stabilizes an adjacent positive charge.<sup>6,7</sup> Although it stabilizes cationic centers orders of magnitude more than a phenyl group, it is somewhat less effective than a phenyl group in stabilizing adjacent radical and carbonionic centers.



The Ferrocene Molecule

A strong attempt has been made to arrange the literature in a functional order useful to the chemist. Necessarily, this attempt is a compromise. For instance, an article reporting the synthesis of acyl ferrocene derivatives may also describe other intermediate compounds or subsequent derivatives. It is necessary to choose a specific section under which to include it. In many cases we have classified a specific paper under two or three headings, but these choices depend on the authors' point-of-view and on limiting the text to an economically reasonable size. Frequently classification of papers into one of the major subdivisions is difficult and the author's viewpoint is followed. Regardless of these obvious shortcomings, we have attempted to provide a document which is easy to use and helpful to the chemist in quickly finding what he needs with a minimum expenditure of time and effort.

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1. T. J. Kealy and P. L. Pauson, A NEW TYPE OF ORGANO-IRON COMPOUND, Nature, London, Vol. 168, 1951, p. 1039.
2. G. Wilkinson, M. Rosenblum, M. C. Whiting, and R. B. Woodward, THE STRUCTURE OF IRON BIS-CYCLOPENTADIENYL, American Chemical Society Journal, Vol. 74, 1952, p. 2125.
3. R. B. Woodward, M. Rosenblum, and M. C. Whiting, THE NEW AROMATIC SYSTEM, American Chemical Society Journal, Vol. 74, 1952, p. 3458.
4. J. Page and G. Wilkinson, THE POLAROGRAPHIC CHEMISTRY OF FERROCENE, RUTHENOCENE AND THE MIDDLE HYDRO-CARBON IONS, American Chemical Society Journal, Vol. 74, 1952, p. 6149.
5. E. M. Arnett and R. D. Bushick, QUANTITATIVE ESTIMATES OF THE STRONG ELECTRON DONOR PROPERTIES OF METAL-LOCENYL NUCLEI, Journal of Organic Chemistry, Vol. 27, 1962, p. 111.
6. E. A. Hill and J. H. Richards, CARBONIUM ION STABILIZATION BY METALLOCENE NUCLEI. II. ALPHA-METALLOCENYL-CARBONIUM IONS. CARBONIUM ION STABILIZATION BY METALLOCENE NUCLEI. III. EVIDENCE FOR METAL PARTICIPATION, American Chemical Society Journal, Vol. 83, 1961, pp. 380 and 4216.
7. D. S. Trifan and R. Bacskai, THE ROLE OF IRON IN CARBONIUM ION REACTION OF FERROCENE DERIVATIVES, Tetrahedron Letters, Vol. 1, No. 13, 1960.

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## Section I. GENERAL STRUCTURE AND THEORY OF FERROCENE REACTIVITY AND BONDING

### A. Ferrocenyl Carbonium Ions

1. Cais, M., Dannenberg, J. J., Eisenstadt, A., Levenberg, M. I., and Richards, J. H.,  
N. M. R. (NUCLEAR MAGNETIC RESONANCE) SPECTRA OF FERROCENYL CARBONIUM IONS, Tetrahedron Letters, No. 15, 1966, pp. 1695-1701.

Nuclear magnetic resonance spectra were determined for a series of  $\alpha$ -R<sup>+</sup>-substituted ferrocenyl carbonium ions (R = CH<sub>2</sub>, Et, CHCHMe<sub>2</sub>, CHCMe<sub>3</sub>, CHPh, CH-p-MeC<sub>6</sub>H<sub>4</sub>, CH-p-MeOC<sub>6</sub>H<sub>4</sub>, CH-p-MeO<sub>2</sub>-CC<sub>6</sub>H<sub>4</sub>, CH-m-MeC<sub>6</sub>H<sub>4</sub>, CH-m-MeOC<sub>6</sub>H<sub>4</sub>, CH-o-MeC<sub>6</sub>H<sub>4</sub>, CH-o-MeOC<sub>6</sub>-H<sub>4</sub>) by using solutions of the respective carbinols in concentrated H<sub>2</sub>SO<sub>4</sub>. The deshielding of the  $\beta$  protons (H-3 and H-4) with respect to the  $\alpha$  protons (H-2 and H-5) and the positions of the peaks assigned to the proton on the carbinyl C are explained on the basis of a structure involving metal participation.

2. Cais, M. and Eisenstadt, A.,  
ORGANOMETALLIC STUDIES. X. REDUCTIVE DIMERIZATION OF  $\alpha$ -METALLOCENYLCARBONIUM IONS. I., Journal of Organic Chemistry, Vol. 30, No. 4, 1965, pp. 1148-1154 (cf. CA 62, 13166h).

Solvolysis of ferrocenylcarbinols followed by reduction with zinc leads to the formation of 1,2-diferrocenylethanes in yields of 60 percent and better. The reaction sequence is envisaged to consist of reduction by zinc of the initially formed  $\alpha$ -ferrocenylcarbonium ion to the ferrocenylcarbinyl radical which upon coupling yields the dimer.

3. Hill, E. A.,  
KINETICS OF THE ETHANOLYSIS OF  $\alpha$ -FERROCENYLETHYL CHLORIDE, Journal of Organic Chemistry, Vol. 28, No. 12, 1963, pp. 3586-3588 (CA 54, 470i).

The extremely rapid solvolysis of  $\alpha$ -ferrocenylethyl chloride was reported. Results obtained were in accord with the high stability of the  $\alpha$ -metallocenyl carbonium ion previously shown in solvolyses of  $\alpha$ -metallocenylcarbinyl acetates.

4. Hill, E. A. and Richards, J. H.  
CARBONIUM ION STABILIZATION BY METALLOCENE  
NUCLEI. III. EVIDENCE FOR METAL PARTICIPATION,  
American Chemical Society, Journal, Vol. 83, 1961, pp. 4216-  
4221 (cf. CA 56, 12941h).

The synthesis and solvolytic behavior of diastereomeric ferrocenylcarbinyl acetates was examined and was interpreted as indicating a direct bonding of the metal atom to the cationic C of the  $\alpha$ -metallocenylcarbonium ions. Thus, 13 g. methylferrocene and 6.62 g.  $\text{Ac}_2\text{O}$  in 150 ml.  $\text{CH}_2\text{Cl}_2$  cooled to  $0^\circ$ , saturated with  $\text{BF}_3$ , stirring continued 1.25 hrs at  $0^\circ$ , the mixture allowed to warm to room temperature during 2.75 hrs, then poured into excess aqueous  $\text{AcONa}$ , sufficient ascorbic acid added to reduce the ferricinium ion, the aqueous phase extracted with  $\text{CH}_2\text{Cl}_2$ , the organic layer washed with saturated aqueous  $\text{NaHCO}_3$ , dried ( $\text{MgSO}_4$ ), and the solvent removed gave a red-brown oil, which in  $\text{C}_6\text{H}_6$ -hexane was chromatographed on 1220 g. acid-washed  $\text{Al}_2\text{O}_3$ . A yellow band containing the starting material was eluted in fraction 1 with  $\text{C}_6\text{H}_6$ -hexane. Development and elution of the monoacetylated products were carried out with  $\text{C}_6\text{H}_6$ - $\text{Et}_2\text{O}$  mixtures. Three methylacetylferrocenes were obtained: (1) 2.07 g., m.  $42.7-3.2^\circ$ ; (2) 1.59 g., m.  $62.2-3.2^\circ$ ; and (3) 1.09 g., m.  $57.5-61.5^\circ$ . Acetylation of 1,1-trimethyleneferrocene gave two isomeric 2,1'-trimethyleneacetylferrocenes, m.  $77.5-8.5^\circ$  and  $100-1^\circ$ . Reduction of 2-methylacetylferrocene with  $\text{LiAlH}_4$  gave two isomeric methyl(2-methylferrocenyl)carbinyl acetates:  $\psi$ -endo, liquid, purified by molecular distribution;  $\psi$ -exo, m.  $54.-5.2^\circ$ . Reduction of  $\alpha$ -oxo-1,2-tetramethyleneferrocene with  $\text{LiAlH}_4$  gave two isomeric  $\alpha$ -hydroxy-1,2-tetramethyleneferrocenes: endo-, m.  $48.5-9.5^\circ$ ; and exo-, m.  $70.5-2^\circ$ . Reduction of 2-acetyl-1,1'-dimethylferrocene with  $\text{LiAlH}_4$  gave two isomeric methyl-(1,1'-dimethyl-2-ferrocenyl)carbinols:  $\psi$ -endo, cloudy orange oil; and  $\psi$ -exo, cloudy oil. The acetates of these were oils. Reduction of 1',2-trimethyleneacetylferrocene with  $\text{LiAlH}_4$  gave two isomeric methyl(1,1'-trimethylene-2-ferrocenyl)carbinols:  $\psi$ -endo, yellow solid, m.  $80-1^\circ$ ; and  $\psi$ -exo, m.  $160-1.5^\circ$ . The corresponding acetates m.  $60-1^\circ$  and  $74.7-5.7^\circ$ , respectively.

5. Kaluski, Z. L. and Struchkov, Y. T.,  
INTERMOLECULAR DISTANCES AND PACKING OF MOLECULES IN THE CRYSTAL OF bis -[1'-(1-ethylferrocenyl)],  
Zhurnal Strukturnoi Khimii, Vol. 7, 1966, pp. 283-286.

Not abstracted.

6. Levenberg, M. I.,  
I. PRELIMINARY STUDIES OF THE CHAIN-TRANSFER CONSTANT OF METHYLFERROCENE, II. PROTONATION OF METALLOCENES, III. AN ANALYSIS OF THE N.M.R. SPECTRA OF SUBSTITUTED FERROCENES, IV. EXPERIMENTAL AND THEORETICAL STUDIES OF THE CHARGE DISTRIBUTION OF THE FERROCENYL CARBINYL CARBONIUM ION, Dissertation Abstract, Vol. 26, April 1966 (Order No. 65-15, 431).

#### PART I

Styrene monomer containing various concentrations of methylferrocene was allowed to polymerize at 70°C. The average molecular weight of the resulting polystyrene was determined, and the chain transfer constant of methylferrocene then calculated. The constant was found to be  $0.7 \times 10^{-4}$ , indicating some contribution to the stability of the methyl free radical by the ferrocenyl group.

The reactivity of methylferrocene to free radical attack is discussed, and the copolymerization of methylferrocene with styrene is considered.

#### PART II

The nuclear magnetic resonance spectra of ferrocene, ruthenocene, and osmocene in boron trifluoride monohydrate have been studied. Accurate measurements of relative peak areas and positions are reported. The species responsible for the nuclear magnetic resonance spectra are discussed.

#### PART III

A detailed analysis of the nuclear magnetic resonance spectra of a series of alkylacetylferrocenes in a variety of solvents has been carried out. This has allowed a determination of the coupling constants between the various protons in these substances. For protons attached to the same ring, the following values are generally observed:  $J_{23} \sim 2.5$  cps and



$J_{24} \sim 1.3$  cps. The magnetic anisotropy of the carbonyl group in 2-acetyl-1, 1'-trimethylene ferrocene is also discussed.

#### PART IV

The existence of the stable ferrocenylcarbinyl carbonium ion has been demonstrated by freezing point depression measurements in concentrated sulfuric acid. The nuclear magnetic resonance spectrum of the carbonium ion has been observed and the chemical shifts of its protons relative to those of methylferrocene have been measured. The factors influencing the proton chemical shifts are discussed.

Techniques of molecular orbital calculations applicable to ferrocenyl systems are discussed and the results of a series of molecular orbital calculations on the ferrocenylcarbinyl carbonium ion are presented. The chemical shifts of the protons on the carbonium ion are predicted from the molecular orbital calculations, and the predictions are compared with the experimentally measured chemical shifts. The agreement is not good as could be desired.

7. Nesmeyanov, A. N., Perevalova, E. G., Gubin, S. P., Grandberg, K. I., and Kozlovsky, A. G.,  
ELECTRONIC PROPERTIES OF FERROCENYL AS A SUBSTITUTE [IN BENZOIC ACIDS], Tetrahedron Letters, 1966, pp. 2381-2387.

Not abstracted.

8. Nesmeyanov, A. N., Sazonova, V. A., Drozd, V. N., and Rodionova, N. A.,  
 $\alpha$ -FERROCENYLCARBONIUM SALTS, Doklady Akademii Nauk SSSR, Vol. 160, No. 2, 1965, pp. 355-358 (In Russian).

Diphenylferrocenylcarbinol (I) in AcOH treated with a trace of HCl gave blue diphenylferrocenylcarbonium ferrichloride (II),  $C_{23}H_{19}Fe_2Cl_4$ , which with aqueous  $Me_2CO$  hydrolyzed, turned yellow and yielded I, m.  $130^\circ$ . II in  $Me_2CO$  treated with a trace of concentrated HCl gave 60 percent 6, 6-diphenylfulvene. I in AcOH and a trace of  $HClO_4$  gave 57 percent diphenylferrocenylcarbonium perchlorate, explodes on heating. Ferrocenylphenylcarbinol similarly treated gave 63 percent brown ferrocenylphenylcarbonium perchlorate. Similar reaction with  $Ph_4BNa$  gave the tetraphenylborate (III), brown solid. This and pyridine gave 88 percent yellow N-(ferrocenylphenylmethyl)pyridinium tetraphenylborate. III heated to  $50^\circ$  in

$\text{MeNO}_2$  gave 42 percent 1, 2-diphenyl-1, 2-diferrocenylethane, m.  $218^\circ$ , and a diastereomet, m.  $275^\circ$ .

9. Nesmeyanov, A. N., Sazonova, V. A., Drozd, V. N., Rodionova, N. A., and Zudkova, G. I.,  
PROPERTIES OF  $\alpha$ -FERROCENYL CARBONIUM IONS,  
Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 11, 1965, pp. 2061-2063 (In Russian).

Phenylferrocenylcarbonium tetraphenylborate and  $\text{PhNMe}_2$  in 10-15 min. at room temperature gave 86 percent p-dimethylaminophenylphenylferrocenylmethane (I), m.  $104^\circ$ , and a similar reaction with diphenylferrocenylcarbonium tetraphenylborate gave 74 percent p-dimethylaminotriphenylferrocenylmethane, m.  $204-6^\circ$ .  $p\text{-Me}_2\text{NC}_6\text{H}_4\text{Li}$  and benzoyl- and benzoylferrocene in  $\text{Et}_2\text{O}-\text{C}_6\text{H}_6$  gave in 0.5 hours 56 percent p-dimethylaminodiphenylferrocenylcarbinol, m.  $101^\circ$ , which with  $\text{Zn}-\text{AcOH}$  was reduced to 75 percent I. The carbinol kept in  $\text{AcOH}$  with a drop of  $\text{HCl}$  gave it 10 min. 38 percent 6-p-dimethylaminophenyl-6-phenylfulvene, m.  $117^\circ$ . Diferrocenyl ketone and  $p\text{-Me}_2\text{NC}_6\text{H}_4\text{Li}$  in  $\text{Et}_2\text{O}-\text{C}_6\text{H}_6$  gave in 40 min. 40 percent p-dimethylaminophenyldiferrocenylcarbinol, m.  $190-2^\circ$  (decomposition), which was reduced as above to p-dimethylaminophenyldiferrocenylmethane, m.  $167.5-8.5^\circ$ .  $p\text{-Me}_2\text{NC}_6\text{H}_4\text{Li}$  and ferrocenylcarboxaldehyde gave 89 percent p-dimethylaminophenylferrocenylcarbinol, m.  $118-18.5^\circ$ , which with  $\text{LiAlH}_4$  in  $\text{Et}_2\text{O}$  reduced to 100 percent p-dimethylaminophenylferrocenylmethane, m.  $137-7.5^\circ$ .

10. Nesmeyanov, A. N., Sazonova, V. A., et. al.,  
ALPHA-FERROCENYL CARBONIUM SALTS (Foreign title not available) Translated into English from Russian by the Foreign Technology Division, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, Report No. FTD-TT-65-43311, AD-615 870, N65-29099, 11 May 1965 (Doklady Akademii Nauk SSSR, Vol. 160, No. 2, 1965, pp. 355-358).

A reaction product, ferrichloride diphenylferrocenylcarbonium, was separated in the destruction of the ferrocene with perchloric acid. At first a dark bluish crystalline salt, insoluble in ester and in benzene, but soluble in acetone and nitromethane, is formed. When water is added to the acetone solution of the salt, the diphenylferrocenylcarbonium intermediate is instantaneously formed. The reaction product is compared to the produce (6 6-diphenylfulvene) obtained when ferrocene is

destroyed with concentrated hydrochloric acid. Other compounds isolated with the ferrocene molecule include relatively stable salts of ferrocenylcarbonium perchlorate and tetraphenylborate (from ferrocenylphenylcarbinol in an acetic acid solution during the action of  $\text{HClO}_4$ , and tetraphenylboronsodium respectively). Thermal decomposition of tetraphenylborate of ferrocenylphenylcarbonium in nitromethane at  $50^\circ$  leads to a mixture of approximately equal amounts of diastereomers 1, 2-diphenyl-1 and 2-diferrocenylethane. Yields, analyses, melting points, and composition analyses for all starting, intermediate, and final compounds are given.

11. Nesmeyanov, A. N., Vol'kenau, N. A., and Bolesova, I. N., REACTION OF FERROCENE WITH SUBSTITUTED AROMATIC COMPOUNDS, Doklady Adakemii Nauk SSSR, Vol. 166, No. 3, 1966, pp. 607-610 (In Russian).

Ferrocene treated with a large excess of an aromatic compound in the presence of 2 moles  $\text{AlCl}_3$  and 1 g. atom Al 3-5 hrs., at  $110-70^\circ$  underwent a displacement reaction of one of the cyclopentadienyl rings by the aromatic ring, forming salts  $[\text{C}_5\text{H}_5\text{FeArH}]^+\text{X}^-$  (ArH and X shown):  $\text{MePh}$ ,  $\text{Ph}_4\text{B}$ , decomposed  $246-6.5^\circ$ ;  $p\text{-C}_6\text{H}_4\text{Me}_2$ ,  $\text{Ph}_4\text{B}$ , decomposed  $253-4^\circ$ ;  $\text{Ph}_2$ ,  $\text{Ph}_4\text{B}$ , decomposed  $225-6^\circ$ ;  $\text{Ph}_2$ ,  $\text{BF}_4$ , decomposed  $134-5^\circ$ ;  $\text{C}_{10}\text{H}_8$ ,  $\text{BF}_4$ , decomposed  $131.5-33^\circ$ ; fluorene,  $\text{Ph}_4\text{B}$ , decomposed  $218-19^\circ$ ;  $\text{AcNHPh}$ ,  $\text{PF}_6$  (I), decomposed  $160.5-2^\circ$ ;  $\text{PhCl}$ ,  $\text{BF}_4$ , decomposed  $214^\circ$ . The yields were 23-40 percent. The salts were yellow to reddish-orange and were soluble in lower alcs. and  $\text{H}_2\text{O}$  for the  $\text{BF}_4$  and  $\text{PF}_6$  salts;  $\text{Ph}_4\text{B}$  salts were insoluble in these solvents but soluble in  $\text{MeCN}$  and  $\text{Me}_2\text{CO}$ . In a typical reaction 5 g. ferrocene and 4.1 g.  $\text{AcNHPh}$  with 22.6 g.  $\text{AlCl}_3$  in decahydronaphthalene under N 5 hrs. at  $115-25^\circ$ , then treated with  $\text{H}_2\text{O}$  at  $0^\circ$ , the aqueous solution treated with  $\text{Na}_2\text{SO}_3$  to reduce the ferriciniumcation, and with aqueous  $\text{NaPF}_6$ , gave I. Reaction with  $\text{PhBr}$  in the presence of  $\text{Al}-\text{AlCl}_3$  at  $60-70^\circ$  gave the product shown above, but in the absence of Al powder the reaction gave a mixture of salts containing  $\text{PhBr}$  and  $\text{C}_6\text{H}_6$  ligands, owing to debrominating action of  $\text{AlCl}_3$ .

12. Nugent, M. J., Jr.,  
PART I:  $\beta$ -FERROCENYLALKYL CARBONIUM IONS, PART II:  
THE STEREOSPECIFIC SYNTHESSES OF THE EXO AND  
ENDO ISOMERS OF  $\alpha$ -HYDROXYMETHYL-1,2-TETRA-  
METHYLENEFERROCENE, University Microfilms (Ann Arbor,  
Michigan), Order No. 65-0935, 167 pp., Dissertation  
Abstracts, Vol. 26, No. 2, 1965, p. 707.

The solvolysis mechanism of  $\beta$ -ferrocenylalkyl tosylates is discussed. Evidence is presented which shows that solvolysis occurs with preferential participation of the inter-annular electrons on the ferrocene moiety leading to intermediate formation of very stable carbonium ions. The products resulting from these solvolysis reactions demonstrate that these carbonium ions exhibit features expected for both ferrocenyl ring-bridged and iron-stabilized intermediates. The stereochemistry of solvolysis of (-)-1-ferrocenyl-2-propyl p-toluene-sulfonate has also been examined and found to occur with complete retention of configuration.

## PART II

The stereospecific syntheses of the exo and endo isomers of  $\alpha$ -hydroxymethyl-1, 2-tetramethyleneferrocene is described.

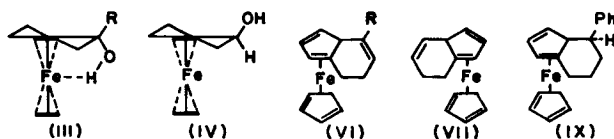
13. Rosenblum, M. and Abbate, F. W.,  
PARTICIPATION OF THE METAL ATOM IN THE REACTIONS  
OF THE IRON GROUP METALLOCENES, Abstracts, 152 ACS  
Meeting, Section 0, No. 138, New York, September 1966.

Participation of the metal atom in the reactions of the iron group metallocenes has been a problem of continued interest and some controversy. The oxidation of these substances undoubtedly involves electron donation by the metal atom, and the dimerization of  $\alpha$ -hydroxyalkylferrocenes, similarly appears to take place by internal electron transfer from the metal atom to an  $\alpha$ -ferrocenylcarbonium ion center. Solvolysis reactions of  $\alpha$ -acetoxyalkylmetallocenes are characterized by their extreme rapidity and high degree of stereoselectivity, both of which attributes have been ascribed to metal atom participation. Alcohol groups in  $\alpha$ - and  $\beta$ -hydroxyalkyl-metallocenes are capable of hydrogen bonding with the metal atom, and in strong acid solutions protonation of the metallocenes apparently takes place at this site. It has also been

supposed that electrophilic ring substitution occurs preferentially through initial formation of an intermediate in which the electrophile is coordinated to the metal atom. Some recent experiments involving stereochemically directed electrophiles are shown to cast doubt on this hypothesis.

14. Schlogel, K. and Fried, M.,  
OPTICALLY ACTIVE HYDROCARBONS OF THE FERROCENE  
SERIES, Tetrahedron Letters, No. 22, 1963, pp. 1473-1478  
(In German).

Cyclization of 4-ferrocenylbutyric acid according to Friedel-Crafts in lieu of with  $\text{CF}_3\text{CO}_2\text{H}$  gave a racemic mixture chiefly of the homoannular ring ketone (I) and 7 percent of the heteroannular 1, 1'-( $\alpha$ -oxotetramethylene) ferrocene (II), m. 100-2°. They were resolved via the diastereomeric (—)-menthylhydrazones, m. 195-6°. The less soluble (+)-ketone (—)-menthylhydrazone,  $[\alpha]_D^{20} 920^\circ \pm 12^\circ$  (c 0.4, all in absolute EtOH), and the more soluble (—)-ketone analog,  $[\alpha]_D^{20} -370^\circ$  (c 0.3), could be qualitatively cleaved with  $\text{H}_3\text{PO}_4$  and HCHO in MeOH, and I and II,  $[\alpha]_D^{22} +$  and  $-540^\circ \pm 5^\circ$  (c 0.3), respectively were regenerated. Reduction of I with  $\text{LiAlH}_4$  gave a 10:1 mixture of endocarinol (III, R = H) (IIIa)  $[\alpha]_D^{22} 40^\circ$  (c 2.8), and exo-carbinol (IV),  $[\alpha]_D^{22} 117^\circ$  (c 0.4), which were separated by thin layer chromatography over silica gel-G and 15:1  $\text{C}_6\text{H}_6$ -EtOH:  $R_F$ , III, 0.60, IV, 0.40. The higher yield of III was explained as resulting from the formation of a H bridge between the OH and the Fe atom, which also explained the more ready oxidation of IV to optically pure I. The difference in  $[\alpha]_D$  of IIIa and IV was caused by the presence of an additional asymmetrical center. Reaction of I with PhLi gave a uniform phenylcarbinol (III, R = Ph) (V),  $[\alpha]_{546}^{22} 300^\circ$ ,  $[\alpha]_D^{22} 190^\circ$ ,  $[\alpha]_{656}^{22} 118^\circ \pm 5^\circ$  (c 0.3). IIIa, IV, the endo-exo-mixture from II, and V were dehydrated by treatment with acid

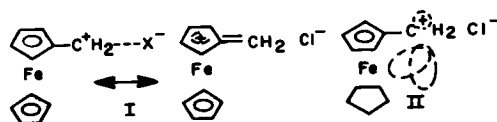


$\text{Al}_2\text{O}_3$  to the corresponding unsaturated hydrocarbons:  
VI (R = H) (VIa),  $[\alpha]_{546}^{22} -2470^\circ$ ,  $[\alpha]_D^{22} -1475^\circ$ ,  $[\alpha]_{656}^{22} -1075^\circ \pm 10^\circ$   
(c 0.1); VII,  $[\alpha]_{546}^{22} 2420^\circ$ ,  $[\alpha]_D^{22} 1458^\circ$ ,  $[\alpha]_{656}^{22} 1020^\circ$  (c 0.3),

both m. 38°,  $\nu$  1620  $\text{cm}^{-1}$   $\lambda_{\text{max}}$  279  $\text{m}\mu$  ( $\epsilon$  6,180), and VI (R = Ph) (VIII), an oil,  $[\alpha]_{546}^{22}$  -1050°,  $[\alpha]_{589}^{22}$  -625°,  $[\alpha]_{656}^{22}$  -438°  $\pm 5^\circ$  ( $c$  0.4),  $\nu$  1645  $\text{cm}^{-1}$ ; vinylferrocene had  $\nu$  1635  $\text{cm}^{-1}$ ,  $\lambda_{\text{max}}$  273  $\text{m}\mu$  ( $\epsilon$  7,440). VIa could be reduced to the asymmetrical 1, 2-tetramethyleneferrocene, m. 30°, which was also obtained on reduction of I with  $\text{LiAlH}_4\text{-AlCl}_3$  (CA 55, 27247i). Reduction of V with  $\text{LiAlH}_4\text{-AlCl}_3$  or of VIII Na-EtOH epimeric exo compound (IX),  $[\alpha]_{546}^{22}$  193°,  $[\alpha]_{\text{D}}^{22}$  126°,  $[\alpha]_{656}^{22}$  87°  $\pm 3^\circ$  ( $c$  0.9), indicating that no change in configuration occurred. Resolution of 1-ethyl-2-acetylferrocene via its menthylhydrazone (m. 151-2°)  $[\alpha]_{\text{D}}^{20}$  -48° ( $c$  1), gave a dextrorotatory ketone, m. 42-3°,  $[\alpha]_{\text{D}}$  0°,  $[\alpha]_{570}^{25}$  25° ( $c$  1), which may not have been quite optically pure and which, reduced with  $\text{LiAlH}_4$  and dehydrated, gave the oily 1-ethyl-2-vinylferrocene,  $[\alpha]_{565}^{22}$  24°,  $[\alpha]_{\text{D}}^{22}$  7°  $\pm 1^\circ$  ( $c$  2.3).

15. Tidwell, T. T. and Traylor, T. G.,  
NUCLEOPHILIC SUBSTITUTION ON FERROCENYLMETHYL  
CHLORIDE, American Chemical Society Journal, Vol. 88,  
1966, p. 3442.

The solvolysis rates of alpha ferrocenylchlorides in ethanol-ether and in sodium ethoxide-ethanol-ether have been compared with the corresponding solvolysis rates of methoxymethylchloride. The rate ratios of these two species for Sn-1 and Sn-2 mechanisms were found to be the same. This was taken as extremely strong evidence that the rate enhancement of alpha ferrocenyl derivatives and the stability of alpha ferrocenyl carbonium ions is due to resonance stabilization (Structure I) and not neighboring group participation (Structure II).



16. Ware, J. C. and Traylor, T. G.,  
RESONANCE STABILIZATION OF CC-FERROCENYL CARBO-  
NIUM IONS, Tetrahedron Letters, 18, 1965, pp. 1295-1302.

The solvolysis rates of a number of alpha ferrocenyl derivatives have been correlated with sigma plus parameters

to show anachimeric assistance by Fe is not the major factor in the stabilization of alpha ferrocenyl carbonium ions. The ferrocenyl group is best considered as a somewhat complexed cyclopentadienide anion in which its ability to supply electrons by resonance is severely decreased by this complexing, but is still so large that its remaining resonance effect on solvolysis rates is about 6 kcal/mole larger than that of a phenyl group.

#### B. Ferricenium Ions and Salts

17. Beckwith, A. L. J. and Leydon, R. J.,  
FREE-RADICAL PHENYLATION OF FERRICENIUM ION,  
American Chemical Society Journal, Vol. 86, 1964, p. 952.

When ferricenium borofluoride (0.011 mole) and phenylazotriphenylmethane (0.011 mole) in acetic acid were maintained at 75° for 1.5 hrs. nitrogen was evolved and the characteristic color of the ferricenium ion faded. The products isolated were phenylferrocene (0.002 mole) and triphenylcarbinol (0.006 mole) together with small amounts of tritylferrocene, triphenylmethane, and tetraphenylmethane. Some ferrocene (0.004 mole) was recovered. Since it has been demonstrated previously that phenylazotriphenylmethane is without effect on neutral ferrocene, there can be little doubt that the formation of phenylferrocene in the present instance represents an authentic example of free-radical phenylation of ferricenium ion.

18. Beckwith, A. L. J. and Leydon, R. J.,  
FREE RADICAL SUBSTITUTION OF FERRICINIUM ION.  
MECHANISM OF THE ARYLATION OF FERROCENE,  
Tetrahedron, Vol. 20, No. 4, 1964, pp. 790-801 (cf. CA 59, 2604 f).

Experiments are described on the reaction of ferrocene (I) with free radical reagents. Thus, 5 g. I, 5.2 g. BzOOBu-tert (II), and 200 ml. C<sub>6</sub>H<sub>6</sub> was refluxed 14 hours under N to give 35 mg. CO<sub>2</sub>, 2.7 g. (BzO)<sub>3</sub>Fe, a trace (BzO)<sub>2</sub>Fe, 1.5 g. BzOH, 2.9 g. I, and unidentified oils. I (4 g.), 12.5 g. II, 200 ml. C<sub>6</sub>H<sub>6</sub>, and 200 ml. N H<sub>2</sub>SO<sub>4</sub> refluxed while the aqueous layer of ferricenium ion (III) was run off and replaced with N H<sub>2</sub>SO<sub>4</sub> at a rate of 10, 3, and 1.4 ml./min. for 6, 5, and 3 hrs., respectively, and III reduced with aqueous TiSO<sub>4</sub> gave 4 g. BzOH

and 3.1 g. I. In similar fashion, I and PhNAcNO gave Ph<sub>2</sub>I, phenylferrocene (IV), and 1, 1'-diphenylferrocene. I did not react with Ph radicals from PhMgBr, Ph<sub>3</sub>CN<sub>2</sub>Ph, PhN<sub>2</sub>Cl. ZnCl<sub>2</sub>, (PhN<sub>2</sub>)<sub>2</sub>SO<sub>4</sub>, or with Me<sub>2</sub>CCN or PhCH<sub>2</sub> radicals. To 5 g. I at 0° was added 25 g. concentrated H<sub>2</sub>SO<sub>4</sub>, the whole kept overnight, diluted with cold EtOH, 8.9 g. azobis (isobutyronitrile) added, the mixture refluxed 4 hours, cooled, H<sub>2</sub>O added, and the brown precipitate chromatographed on alumina and eluted with petr. ether to give 0.4 g. 2-cyano-2-ferrocenylpropane (IVa), m. 63-4° (petr. ether). To NaNH<sub>2</sub> (from 1.3 g. Na in 100 ml. liquid NH<sub>3</sub>) was added 11 g. ferroceneacetonitrile, then 7.5 g. MeI, the NH<sub>3</sub> allowed to evaporate and the Et<sub>2</sub>O solution refluxed 2 hrs. to give 8.4 g. crude 1-cyano-1-ferrocenylethane (V); since the V could not be purified, 6.9 g. V was retreated with NaNH<sub>2</sub> and MeI to give 4.3 g. IVa. To 5 g. I, 5.3 g. anhydrous FeCl<sub>3</sub>, 130 ml. PhMe, and 65 ml. AcOH was added 15.7 g. II in 6 hrs. under N and the whole stirred 7 hrs. at 70° to give 1.3 g. benzylferrocene (VI), m. 74-5° aqueous EtOH). To 5 g. I and 200 ml. PhMe was added 22.3 g. II under N in 1 hr. and the whole kept 6 hrs. at 70-80° to give 100 mg. VI. When 0.9 g. I and 0.5 g. anthracene was treated with benzenediazonium borofluoride in Me<sub>2</sub>CO, the products were 3.2 mg. 9-phenylanthracene and 100 mg. IV. The mechanisms of the reactions are discussed.

19. Beckwith, A. L. J. and Leydon, R. J.,  
THE MECHANISM OF THE REACTION OF FERROCENE WITH  
FREE-RADICAL REAGENTS, Tetrahedron Letters, No. 6,  
1963, pp. 385-388.

The recent publication of a mechanism for the arylation of ferrocene involving formation of a charge-transfer complex prompts us to report the results of our investigation into the reactions of ferrocene with free-radical reagents.

Ferrocene in benzene, when treated with benzoyl peroxide or with t-butyl perbenzoate, gave ferric benzoate in high yield. Negligible quantities of carbon dioxide were evolved. The intermediate formation of ferricinium ion in these reactions was demonstrated by conducting the experiments in an apparatus designed to allow continuous extraction of the mixture with dilute sulphuric acid. Up to 78 percent of the ferrocene was then extracted as ferricinium ion and the yield of ferric benzoate was reduced accordingly.



20. Brandon, R. L., Osiecki, J. H., and Ottenberg, A.,  
REACTIONS OF METALLOCENES WITH ELECTRON ACCEPTORS, Journal of Organic Chemistry, Vol. 31, No. 4, 1966, pp. 1214-1217.

The reaction products of ferrocene, cobaltocene, and bis (tetrahydroindenyl) iron with 2, 3-dichloro-5, 6-dicyanoquinone and tetracyanoethylene (I) were isolated and their physical properties, including infrared spectra, visible spectra, and electrical resistivities, were detected. The equilibrium constructions for the reaction, metallocene + I = metallocinium + I<sup>-</sup>, were measured in various solvents. The relation between the oxidation-reduction potentials of the metallocenes and the properties of the products is discussed.

21. Dove, M. F. A. and Sowerby, D. B.,  
REACTION OF METALLOCENES WITH THIOCYANOGEN, Zeitschrift fur Naturforschung, Vol. 20b, No. 4, 1965, pp. 394-395.

An Et<sub>2</sub>O solution of (SCN)<sub>2</sub> was added slowly to a solution of ferrocene to give a dark brown, unidentified powder, which was not a simple thiocyanate, although ferricinium ions were present. Using CH<sub>2</sub>Cl<sub>2</sub> as solvent a dark-colored crystalline product [(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Fe]<sub>2</sub>Fe(NCS)<sub>4</sub> precipitated. Infrared spectra showed strong bands at 3095, 1414, 1010, and 850 cm.<sup>-1</sup> characteristic of the ferricinium ion and at 2055, 480, and 262 cm.<sup>-1</sup> due to the iron thiocyanate group. The electronic spectrum in a KBr disc showed a strong maximum at 20.3 kK with a shoulder at 15.8 kK. An analogous reaction between cobaltocene and (SCN)<sub>2</sub> in Et<sub>2</sub>O at room temperature yielded as the main product yellow crystalline cobalticinium thiocyanate as shown by elemental analysis, infrared and electronic spectra, conductivity, and proton nuclear magnetic resonance.

22. Kalle, A.  
HEAT-FIXABLE LIGHT-SENSITIVE FERROCENE LAYERS, Neth. Appl. 6,504,126 (Cl. G 03c), 18 October 1965, Ger. Appl. 15 April 1964, 8 pp.

Mixtures of ferrocene and halogenated hydrocarbons (CBr<sub>4</sub>) are known to react under the influence of γ-radiation to form ferrocinium tetrahalogen ferrates. Such mixtures can also be used to form brown negative prints upon exposure to

ultraviolet radiation or visible light, and these can be fixed by heating at 80-120°, which causes evaporation of the unreacted components. The light-sensitivity of the systems is improved in the presence of amines or phenols which form dyes when exposed with CBr<sub>4</sub>. Substituted ferrocenes, e. g., diacetylferrocene, can also be used, and synthetic resins or waxes to improve adhesion of the coatings to smooth-surfaced supports. In an example, paper is impregnated with a solution containing 3 g. each of ferrocene and CBr<sub>4</sub> and 0.1 g. 1-naphthylamine dissolved in a mixture of 15 cc. each of Me<sub>2</sub>CO and trichloroethylene, exposed after drying, for 15 sec. through a transparency to a 200-w. W lamp, and passed by an infrared source, yielding a brown-violet copy.

23. Nesmeyanov, A. N., Materikova, R. B., Kochetkova, N. S., and Tsurgozen, L. A.,  
1, 1'-DIALKYLCOBALTICINIUM SALTS, Doklady Akademii Nauk SSSR, Vol. 160, No. 1, 1965, pp. 137-138 (in Russian).

1, 1'-Diethylferrocene in EtNH<sub>2</sub> added to Li shavings (excess) and kept 10-12 min. under N with dry-ice-cooling gave, after treatment with dry CoBr<sub>2</sub> in tetrahydrofuran, warmed to 20°, then hydrolyzed at 3-5°, some diethylferrocene, and the aqueous layer treated with HBr gave an oily precipitate, which washed with HBr-Br, then shaken with Ag<sub>2</sub>O 12 hrs. and finally treated with HCl gave 6 percent 1, 1'-diethylcobalticinium chloroplatinate, m. 187-7.5°. Similarly prepared was its dipropyl analog, 18 percent, m. 208.5-209°; the latter and HgCl<sub>2</sub> gave the mercuric trichloride salt, m. 84.5-85°.

24. Nesmeyanov, A. N., Yur'eva, L. P., Materikova, R. B., and Hetnarski, B.,  
STABILITY OF SOME FERRICINIUM SALTS, Izvestia Akademii Nauk, SSSR Seriya Khimicheskaya, No. 4, 1965, pp. 731-733 (In Russian).

Ferrocene and iodine in EtOH at 50° gave black ferricinium triiodide, decomposed 169-71°. Br similarly gave at -20° in C<sub>6</sub>H<sub>6</sub>-heptane 43 percent tribromocyclopentene, m. 63-4°; the residual salt treated with H<sub>2</sub>O and Na<sub>2</sub>SO<sub>4</sub> gave 52 percent ferrocene; bromination at -30° gave blue-green ferricinium perbromide, C<sub>10</sub>H<sub>10</sub>FeBr<sub>3</sub>, a very unstable solid, which decomposed in air at 20°. Ferrocene and Cl in CHCl<sub>3</sub> at -40° gave ferricinium ferrichloride; SO<sub>2</sub>Cl<sub>2</sub> at -5° also gave this salt,

while at  $-80^{\circ}$  a solid approximating the composition of ferricinium trichloride was obtained. Ferrocene and dioxane- $\text{Br}_2$  at  $-80^{\circ}$  gave ferricinium tribromide. Ferrocene and p-benzonquinone in  $\text{Et}_2\text{O}$  treated with dry  $\text{HCl}$  gave a precipitate of ferricinium chloride. Ferricinium tribromide in  $\text{AcOH}$  was converted into ferricinium ferribromide.

25. Pavlik, I., Machacek, J., Stibr, B., and Soehnel, O.,  
NOVEL FERRICINIUM SALTS, Sb. Ved. Praci, Vysoka  
Skola Chem. Technol., Pardubice, No. 2, 1964, pp. 37-43  
(In Czechoslovakina).

The preparations by known procedures and some properties of ferricinium triiodide, pentaodobismutite, tetrachloroaluminate, and hexachlorostannate are described. The weakening of the iron-to-cyclopentadienyl ring bond in the ferricinium cation in comparison with ferrocene and the strengthening of the C-C bonds in the cyclopentadienyl rings are confirmed by interpretation of infrared spectra.

26. Pavlik, I. and Plechacek, V.,  
UBER DAS IR-SPEKTRUM VON DEUTERIERTEM FERRICINIUM,  
Collection of Czechoslovak Chemical Communications,  
Vol. 31, No. 5, 1966, p. 2083.

Within the framework of oscillation spectrum studies of the ferricinium cation, we investigated the infrared spectrum of the ferricinium - d - 10 cation. The infrared absorption bands were contributed to the infrared active fundamental oscillations. The validity of the assumption was tested by calculating the deuterium factors of the specific oscillations and with the aid of the Teller-Redlich product for oscillations of the same type of symmetry. At the same time we defined several fundamental frequencies of the oscillations, and found significant qualitative differences in the intensities of the absorption bands of specific fundamental oscillations between ferrocene and ferricinium - d - 10 conditions the frequency of several fundamental oscillations of the cation are displaced, in comparison to the frequencies of the same oscillations in the neutral molecule.

27. Pavlik, I. and Zizek, V.,  
ACETYLFERRICINIUM SALTS, Collection of Czechoslovak  
Chemical Communications, Vol. 31, No. 5, 1966, p. 1985,

Acetylferricinium salts (tetrachloroferrate, reineckate and tungstosilicate) were prepared for the first time by oxidizing acetylferrocene. The presence of acetylferricinium was confirmed by chromatographic analysis of the products of the reduction of the salts and the infrared spectra which contain the characteristic absorption bands of ferricinium and of the acetyl group. Some fundamental frequencies of the ferricinium nucleus of acetylferricinium are shifted against acetylferrocene, in a similar way as the corresponding frequencies of ferricinium against ferrocene. The blue shift of the frequency  $\nu$  (C = O) and the red shift of  $\nu$  (C<sub>ring</sub> - C<sub>acetyl</sub>) shows that the carbonyl group of the acetyl in acetylferricinium is less conjugated with the ferricinium nucleus than in acetylferrocene with the ferrocene nucleus.

28. Shanks, D. R.,  
Title not available, Inorg. Syn., Vol. 7, 1963, p. 201.

The preparation of ferrocene ( $\text{Fe}^{55}$  and  $\text{Fe}^{59}$ ) by bombarding inactive ferrocene with neutrons and utilizing the high retention of  $\text{Fe}^{55}$  and  $\text{Fe}^{59}$  as ferrocinium salts which is converted to ferrocene is described. The procedure involves irradiating ferrocene with a large fast neutron flux for six days followed by a two-day "cooling" period. A 95 percent yield of ferrocene of 20 percent isotopic  $\text{Fe}^{59}$  yield is obtained. Higher neutron fluxes gave higher activity.

The preparation of  $\text{Fe}^{59}$  labeled ferricinium perchlorate from  $\text{Fe}^{55}$   $\text{Fe}^{59}$  labeled ferrocene in the anode compartment of an electrolytic cell is described. The cathode compartment contains 0.1 M perchloric acid. The decomposition of ferrocene and ferricinium salts in concentrated  $\text{HNO}_3$  and electrodeposition of Fe on copper disks is described.

29. Shustorovich, E. M. and Dyatkina, M. E.,  
THE ELECTRONIC STRUCTURE OF FERROCENE, Zhurnal  
Strukturnoi Khimii, Vol. 7, No. 1, 1966, pp. 135-140  
(In Russian), Chemistry of the Iron Group Metallocenes: Ferrocene, Ruthenocene, Osmocene, New York, New York, J. Wiley and Sons, Pt. 1, 1965, p. 23.

Rosenblum states that, according to Shustorovich and Dyatkina, the electron removed during the transformation of

the ferrocene molecule into a ferricinium ion is detached from ring orbitals rather than from the metal and that this is improbable from the energy standpoint as well as contrary to results of study of the Moessbauer effect. Actually, these authors concluded that the electron is removed from the upper occupied molecule orbital ( $e_{2g}$ ), which consists of  $\sim 75$  percent of the 3d orbital of Fe, whereupon redistribution of the electronic d. takes place, so that the effective charge of the Fe atom in the ferricinium cation remains the same as in ferrocene. This process is favored from the energy standpoint because of the excess electron d. in the ring. Calculations based on it lead to a correct prediction of the experimental observed phenomena involving the Moessbauer effect. Rosenblum refers to the position of loosening molecule orbitals which, in his opinion, does not explain the transfer of the charge between Fe and the ring on the basis of spectra of ferrocene and its derivatives as satisfactorily as the location of levels proposed by Dahl and Ballhausen (CA 61, 1379g). Here a misunderstanding has occurred because of the fact that Rosenblum interprets the absorption bands on the basis of virtual energies of loosening molecule orbitals, which lack direct physical meaning in Roothaan's method (CA 46, 7382c). The energy of transition from an occupied orbital  $\Psi_m$  to a free orbital  $\Psi_m$  is not equal simply to the difference in the energies of these orbitals  $\epsilon_k - \epsilon_m$ , but to  ${}^1,3E_{mk} = \epsilon_k - \epsilon_m (J_{mk} - K_{mk}) \pm K_{mk}$ , where  $J_{mk}$  and  $K_{mk}$  are the Coulomb and exchange integral, respectively, with the participation of the two orbitals and a plus sign refers to the singlet state, while a minus sign refers to the triplet state. By applying calculations of the type used by S. and D. (CA 58, 7386f), the observed bands in the ultraviolet absorption spectrum of ferrocene can be explained.

30. Stukan, R. A. and Yur'eva, L. P.,  
THE INVESTIGATION OF FERRICINIUM FERRICHLORIDE  
BY NUCLEAR- $\gamma$ -RESONANCE METHOD, Doklady Akademii  
Nauk SSSR (Chemistry Section), Vol. 167, 1966, pp. 1311-1313  
(In Russian).

Not abstracted.

31. Goan, J. C., Berg, E., and Podall, H. E.,  
NOVEL COMPLEXES OF METALLOCENES WITH  $\pi$ -ACCEPTORS, Journal of Organic Chemistry, Vol. 29, No. 4, 1964, pp. 975-977.

Ferrocene, nickelocene, and cobaltocene reacted quite rapidly with benzoquinone and other  $\pi$ -acceptors to form a series of complexes. Stable complexes except with ferrocene were isolated with these  $\pi$ -acceptors. The properties, infrared spectra, and electron spin resonance spectra were studied of these isolable complexes. It appeared that the ease of forming isolable complexes of metallocenes with  $\pi$ -acceptors correlated with the electron donor-acceptor properties of the components. Simple charge transfer between the  $\pi$ -cyclopentadienyl ring and  $\pi$ -acceptor did not appear evident.

32. Hetnarski, B.,  
COMPLEXES OF SOME FERROCENE DERIVATIVES WITH S-TRINITROBENZENE AND PICRYL CHLORIDE, Bull. Acad. Polon. Sci., Ser. Sci. Chim., Vol. 13, No. 9, 1965, pp. 557-561.

Complexes of s-trinitrobenzene with chloromercuriferrocene, ethylferrocene, and 1, 1'-dipropylferrocene and the complex of picryl chloride with ethylferrocene in  $(CH_2Cl)_2$  are described. The kind of substituent in the ferrocene molecule determines the shift of the complex absorption band maximum. An electron-attracting substituent (chloromercuric group) causes a hypsochromic shift, whereas electron-repelling groups (Et or Pr) cause a bathochromic shift, as compared with complexes in which ferrocene is a donor. The ionization potentials for ferrocene derivatives and for derivatives of other metallocenes in general are reported. Substitution on the ferrocene molecule has a double effect on the value of the equilibrium constant for complex formation. It diminishes the value of the equilibrium constant by steric hindrance and exerts an inductive effect on the reaction center of the ferrocene molecule, causing a change of its electronic density. This effect diminishes the value of the equilibrium constant in the case of electron-attracting substituents and increases their value in the case of electron-repelling substituents. In the chloromercuriferrocene molecule, both effects act in the same direction, diminishing the equilibrium constant in comparison with the value for the complex with ferrocene as

donor. In ethylferrocene, these effects are opposite so they essentially cancel one another. In 1, 1'-dipropylferrocene, an appreciable decrease of the amount of energy necessary for charge transfer is observed.

33. Hetnarski, B.,  
PROPERTIES OF FERROCENE COMPLEXES WITH  
TRINITROBENZENE DERIVATIVES. II., Bull. Acad. Polon.  
Sci., Ser. Sci. Chim., Vol. 13, No. 8, 1965, pp. 515-521.

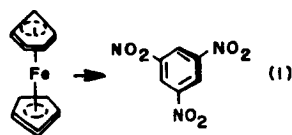
The appearance of a new absorption band in the visible spectra of compounds of ferrocene with trinitrobenzene derivatives indicates these compounds to be charge-transfer complexes. The equilibrium construction for the formation of organic charge-transfer complexes diminishes as the dielectric construction of the reaction medium is raised. As a further test of the nature of metallocene complexes, the equilibrium construction for the ferrocene complexes with s-trinitrobenzene, picryl chloride, and picric acid as acceptors was investigated in  $\text{CH}_2\text{ClCH}_2\text{Cl}$ ,  $\text{CHCl}_3$ ,  $\text{CCl}_2:\text{CCl}_2$ , and  $\text{CHCl}:\text{CCl}_2$  solvents at  $23^\circ$ . The absorption data obey the Benesi-Hildebrand equation,  $1/\bar{\epsilon} = (1/C)(1/K_x\epsilon) + 1/\epsilon$ , where  $\bar{\epsilon}$  is the formal molar extinction coefficient of the acceptor,  $K_x$  is the complex formation equilibrium construction,  $\epsilon$  is the molar extinction coefficient of the complex, and C is the donor (ferrocene) concentration. The data indicate that only 1 complex is present. The  $K_x$  value diminishes as the dielectric construction of the solvent is raised. The relation of the respective  $K_x$  values for ferrocene-s-trinitrobenzene and ferrocene-picryl chloride complexes vary linearly with the dielectric construction of the solvent. The solvent does not affect the molar extinction coefficient or the absorption maximum of the complexes. For the ferrocene-s-trinitrobenzene complex, the enthalpy  $\Delta H^\circ = -1.8 \pm 0.6$  kcal/mole, free energy of formation  $\Delta G^\circ = -0.61 \pm 0.07$  kcal./mole, and  $T\Delta S^\circ = -1.2 \pm 0.6$  kcal./mole for the  $\text{CH}_2\text{ClCH}_2\text{Cl}$  solution. When two or more isomers of the 1:1 complex are present in the solution, the molar extinction coefficient for the complex is a function of temperature. Data at  $4^\circ$  and  $30^\circ$  show no difference in the molar extinction coefficient. This is further evidence that only one isomeric form is present in the complexes investigated.

4. Hetnarski, B.,  
PROPERTIES OF FERROCENE COMPLEXES WITH  
TRINITROBENZENE DERIVATIVES. III., Bull. Acad. Polon.  
Sci., Ser. Sci. Chim., Vol. 13, No. 8, 1965, pp. 523-526.

Charge-transfer complexes of ferrocene with 1-chloro-2, 4-dinitrobenzene, p- and m-dinitrobenzene as acceptors were studied to establish the effect of the reduced number of ring-substituted nitro groups on the absorption band maximum position, complex formation equilibrium construction, and molar extinction coefficient at the charge-transfer band maximum wavelength. Job-type plots showed the constituents to be present in equimolar ratios in the complexes. As was the case with the trinitro derivatives, the absorption maximum for the dinitro derivatives occurred at 535 m $\mu$ . The equilibrium construction for formation of the complexes and their molar extinction coefficients in CH<sub>2</sub>ClCH<sub>2</sub>Cl solution were determined by using the Benesi-Hildebrand equation. The  $K_x$  and  $\epsilon_{\max}$  were, respectively: 1-chloro-2, 4-dinitrobenzene,  $2.0 \pm 0.4$ , 211; p-dinitrobenzene,  $2.0 \pm 0.2$ , 277; m-dinitrobenzene,  $1.8 \pm 0.3$ , 206. The equilibrium construction for the ferrocene-s-trinitrobenzene complex formation,  $K_x = 2.8$ , is about 1.33 times the formation construction of ferrocene complexes with dinitrobenzene derivatives. The molar extinction coefficient for the dinitrobenzene derivative complexes are much lower than those of the trinitrobenzene derivative, e.g., s-trinitrobenzene  $\epsilon_{\max} = 630$ . Temperature had no effect on  $\epsilon_{\max}$ .

35. Hetnarski, B.,  
STERIC CONFIGURATION OF MOLECULES IN CHARGE-TRANSFER COMPLEXES OF FERROCENE WITH NITROBENZENE DERIVATIVES, Bull. Acad. Polon. Sci., Ser. Sci. Chim., Vol. 13, No. 9, 1965, pp. 563-569.

The structure (I) of the charge-transfer complex of ferrocene with 1, 3, 5-(O<sub>2</sub>N)<sub>3</sub>C<sub>6</sub>H<sub>3</sub> was suggested as probable. The acceptor molecule is situated symmetrically with respect to the ferrocene molecule, shields the Fe atom surrounded by the  $\pi$ -electrons, and overlaps the orbitals between the cyclopentadienyl rings. The ferrocene ionization potential





was associated with an electron situated between the cyclopentadienyl rings, and the ionization potential was connected with the position of the charge-transfer band.

36. Rosenblum, M., Fish, R. W., and Bennett, C.,  
THE PROPERTIES OF A FERROCENE-TETRACYANOETHYLENE CHARGE-TRANSFER COMPLEX, American Chemical Society Journal, Vol. 86, No. 23, 1964, pp. 5166-5170.

The complex of ferrocene with tetracyanoferrocene (I), recently reported by Webster, et al. (CA 58, 5722d), and formulated by them as a ferricenium salt on the basis of its properties in solution, is shown instead to be a charge-transfer complex. The green 1:1 complex exhibits charge-transfer absorption at 975 and 1150 m $\mu$  in the solid state and at 900 and 1075 m $\mu$  in cyclohexane. Preliminary studies suggest that similar complexes are formed by substituted ferrocenes. The physical properties of the ferrocene-I complex including its infrared, visible, and ultraviolet spectra and its magnetic susceptibility have been determined. Association constructions and molar extinction coefficients for I complexes of ferrocene, benzene, and pentamethylbenzene in cyclohexane have been measured. Possible structures of the complex are discussed.

37. Watanabe, H., Motoyama, I., and Hata, K.,  
ELECTRICAL PROPERTIES OF METALLOCENES AND THEIR DERIVATIVES, Chemical Society of Japan. Bulletin, Vol. 39, No. 850, 1966.

Not abstracted.

#### D. Protonated Ketones

38. Rubalcava, H. E. and Thomson, J. B.,  
A SPECTROSCOPIC STUDY OF THE PROTONATION OF ACYLFERROCENES, Spectrochimica Acta, Vol. 18, 1962, pp. 449-459.

The changes in the infrared spectra of formylferrocene (I), acetylferrocene (II), and 1, 2- ( $\alpha$ -oxotetramethylene) ferrocene (III) in the presence of gaseous HCl or DCl indicate protonation of the carbonyl O. It is postulated that the Fe helps to stabilize the protonated species. The postulate is supported by the observations that under similar conditions ferrocene, benzaldehyde, tetralone, anthrone, and acetone were not measurably protonated, indicating that neither the ferrocene

residue nor ketone alone were responsible; 1, 1'-( $\alpha$ -oxotrimethylene) ferrocene, in which the requisite orientation cannot be achieved, shows very little reaction; and both the O-H and C:O frequencies ( $\sim 2200$  and  $\sim 1550$   $\text{cm}^{-1}$ , respectively) in protonated I, II, and III indicate bonds which are weaker than normal. No evidence for a C-Cl bond was observed.

39. Rubalcava, H. E. and Thomson, J. B.,  
A SPECTROSCOPIC STUDY OF THE PROTONATION OF  
ACYLFERROCENES. II. HYDROGEN-DEUTERIUM EXCHANGE  
IN THE CONJUGATE ACIDS, Journal of Physical Chemistry,  
Vol. 67, 1963, pp. 301-303 (cf. CA 58, 8532 g).

Infrared spectra of the products formed in the reaction between-HCl or DCl and the bases acetylferrocene and 1, 2-( $\alpha$ -oxotetramethylene)-ferrocene are discussed with particular reference to H-D exchange in the conjugate acids of the ketones. The results indicate that isotopic exchange occurs at the acyl C atoms next to the carbonyl group, but not on the unsubstituted rings.

#### E. Resonance and Inductive Effects

40. Benkeser, R. A., Nagai, Y., and Hooz, J.,  
ELECTRONIC AND STERIC EFFECTS IN MONOSUBSTITUTED  
FERROCENES AS DETERMINED BY RELATIVE SITE  
REACTIVITIES AND DESILYLATION, American Chemical  
Society Journal, Vol. 86, No. 18, 1964, pp. 3742-3746.

Site reactivities relative to both the 1'-position and to a position in ferrocene itself were determined for the monoacylation of methyl-, ethyl-, isopropyl-, and tert-butylferrocene. The detriethylsilylation rates for 1'-methyl-, 1'-isopropyl-, and 1'-tert-butyltriethylsilylferrocene. The results indicate that the 3-position in an alkylferrocene is activated with respect to both the 1'-position as well as to a position in unsubstituted ferrocene. This activation is in the inductive order  $\text{tert-Bu} > \text{iso-Pr} > \text{Et} > \text{Me}$ . One can also conclude with assurance that the presence of an alkyl group does activate a 1'-position relative to a position in unsubstituted ferrocene. While these "interannular" effects are in the order indicative of resonance interactions ( $\text{Me} > \text{Et} > \text{iso-Pr} > \text{tert-Bu}$ ) one is not justified in drawing this conclusion from the data since the desilylation results indicate there could exist hitherto unrecognized steric factors operating between the ferrocene rings during electrophilic substitution.

41. California University, Department of Chemistry, San Diego, California,  
RESONANCE STABILIZATION OF ALPHA-FERROCENYL CARBONIUM IONS, REVISED EDITION by J. C. Ware and T. G. Traylor, March 1965, Report No. AFOSR-65-1669, Contract No. AF-AFOSR-514-64, AD-624-364 (Tetrahedron Letters, No. 18, 1965, pp. 1295-1302) (Unclassified Report).

It is shown that the ferrocenyl group is best considered as a somewhat complexed cyclopentadienide anion in which its ability to supply electrons by resonance is severely decreased by this complexing.

The remaining resonance effect on solvolysis rates is about 6 kcal. /mole larger than that of a phenyl group. Although the iron atom could bond to the alpha-carbon after the ratelimiting step to govern stereochemistry, the stereospecificity of these reactions can be explained on the basis of steric effects.

42. Grandberg, K. I. and Gubin, S. P.,  
ABSORPTION SPECTRA OF HETEROANNULAR DISUBSTITUTED FERROCENES, Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, 1966, pp. 551-554.

Not abstracted.

43. Grandberg, K. I., Gubin, S. P. and Perevalova, E. G.,  
EFFECTS OF SUBSTITUENTS ON THE ABSORPTION BAND SHIFTS IN THE SPECTRA OF MONOSUBSTITUTED FERROCENE, Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, 1966, pp. 549-551.

Not abstracted.

44. Grandberg, K. I. and Kost, A. N.,  
PYRAZOLES. XXVIII. BASICITY OF PYRAZOLES CONJUGATED WITH VARIOUS AROMATIC SYSTEMS (THE PECULIARITY OF THE FERROCENE AROMATIC SYSTEM), XXIX. THE POSSIBILITY OF A CALCULATION OF RELATIVE BASICITIES OF PYRAZOLES, Zhurnal Obshchei Khimii, Vol. 32, 1962, pp. 3025-3033 (CA 58, 4537f, 9039a).

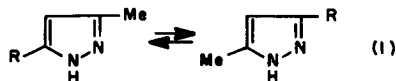
#### XXVIII

Acetylferrocene and  $\text{NaNH}_2$  in refluxing  $\text{Et}_2\text{O}$  0.5 hr., followed by 1 hr. with  $\text{EtOAc}$ , gave a precipitate of di-Na salt of the diketone, which on acidification gave 20 percent acetylacetoferrocene, m.  $94.5-5.5^\circ$ . Refluxing the appropriate diketones

with  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$  in EtOH 1 hr. gave the following I (percent yield, R, m. p. given): 78,  $\alpha$ -selenophenyl (I), 115-16°; 86,  $\alpha$ -thienyl (II) 134.5° (Parrini, CA 52, 3784b) (picrate m. 139.5°); 82,  $\alpha$ -furyl (III), 91°; 84, Ph (IV), 126°; 51, (b. 204°,  $n_D^{20}$  1.4931,  $d_{20}$  1.0128; picrate m. 142°); 87 Me (VI) 107°; and 68, ferrocenyl VII, 162-3°. The following pH values were determined for solutions of the pyrazoles in the form of sulfates in aqueous MeOH (concentration not stated): I, 1.23; II, 1.32; III, 1.48; IV, 1.60; V, 2.45; VI, 3.12; VII, 2.89. Ultraviolet spectra of the pyrazoles were reported. The bathochromic shift in these spectra was directly dependent on the degree of conjugation of the ring substituents with the pyrazole ring. The results indicated a very weak interaction of the ferrocene electronic system with electrons of the pyrazole ring.

## XXIX

The pH values of solutions of substituted pyrazoles follow the equation  $\text{pH}_x = \text{pH}_0 \times K_x$ , where  $K_x$  is a proportionality coefficient which characterizes a substituent in the ring. For unsubstituted pyrazole in aqueous MeOH,  $\text{pH}_0$  is 1.87, which may be used as the point of reference. For polysubstituted pyrazoles the proper number of  $K_x$  coefficients are used as the multipliers in the above equation. The following pH values are observed for 95 percent aqueous MeOH solutions of substituted pyrazoles in the form of sulfates (substituents given): 3, 5-dimethyl-4-benzyl, 3.02; 3, 4, 5-trimethyl, 3.47; none, 1.87; 3, 5-dimethyl-4-acetyl, 0.92; 3, 5-dimethyl, 3.12; 1-phenyl-3, 5-dimethyl, 1.36; 4-bromo, 0.68; 3, 5-dimethyl-4-bromo, 1.12. The following values of  $K_x$  were determined for 4-substituted 1-heptyl-3, 5-dimethylpyrazoles (substituent shown): H, 1.00; Me, 1.19; Et, 1.16; Pr, 1.145; Bu, 1.14;  $\text{PhCH}_2$ , 0.97;  $\text{AcNH}$ , 0.58;  $\text{BzNH}$ , 0.41;  $\text{CHO}$ , 0.40; I, 0.36; Br, 0.31; Cl, 0.30; Ac, 0.28; Bz, 0.255;  $\text{EtO}_2\text{C}$ , 0.245; NO, 0.24; and  $\text{NO}_2$ , 0.21. Similar values for 4-substituted 1, 3, 5-trimethylpyrazoles are given: H, 2.54, Me, 2.96, Ac, 0.68, Bz, 0.59,  $\text{NO}_2$  0.48; for 3(5)-substituted-3(5)-methylpyrazoles: H, 1.00; Me, 1.27; ferrocenyl, 1.18; EtO, 1.07; Ph, 0.666; 2-furyl, 0.605; 2-thienyl, 0.54; 2-selenophenyl, 0.505; and for 1-substituted 3, 5-dimethylpyrazoles: H, 1.000, Me, 0.815, iso-Pr, 0.81, Pr, 0.805, cyclohexyl, 0.775,  $\text{C}_7\text{H}_{15}$ , 0.755,  $\text{PhCH}_2\text{CH}_2$ , 0.74,  $\text{C}_8\text{H}_{17}$ , 0.695,  $\text{C}_{12}\text{H}_{25}$ , 0.685,  $\text{CH}_2$ :  $\text{CHCH}_2$ , 0.675,  $\text{C}_{16}\text{H}_{33}$ , 0.64,  $\text{C}_{18}\text{H}_{37}$ , 0.63,  $\text{PhCH}_2$ , 0.56,  $\text{NCCH}_2\text{CH}_2$ , 0.515, Ph, 0.435,  $\text{HOCH}_2$ , and 0.165. The coefficients shown give calculated pH values for such solutions of substituted pyrazoles which were usually within 10 to 12 percent of observed values.



45. Gubin, S. P., Grandberg, K. I., Perevalova, E. G., and Nesmeyanov, A. N.,  
 TRANSANNULAR ELECTRONIC EFFECTS IN FERROCENYL NUCLEUS. DISSOCIATION CONSTANTS OF SUBSTITUTED FERROCENECARBOXYLIC ACIDS, Doklady Akademii Nauk SSSR, Vol. 159, No. 5, 1964, pp. 1075-1078 (in Russian).

The following values of dissociation constants were obtained from potentiometric data at 25° by titration in 50 percent EtOH with alcohol NaOH (values given as  $K \times 10^7$ ) (substituent shown): Pr, 4.5; Bu, 4.7; Et, 5.0;  $\text{PhCH}_2$ , 5.5; H, 8.1; MeO, 8.5; Cl, 12.6; Br, 12.6;  $\text{CO}_2\text{Me}$ , 16.5; COEt, 21.4; COPr, 21.9; Bz, 23.4; Ac, 25.7; and CN, 36.0. These values were discussed in relation to the Hammett substituent constructions. Except for the halogens, the substituents in ferrocenecarboxylic acids affect the dissociation constant only by their inductive effects and the ferrocene nucleus evidently inhibits a transmission of conjugation effects.

46. Hoh, G. L. K.,  
 STUDIES AT CONSTANT CURRENT, PART I. SUBSTITUENT EFFECTS IN THE CHRONOPOTENTIOMETRIC OXIDATION OF FERROCENES, PART II. THE POLYMERIZATION OF STYRENE AT A CATHODE, University Microfilms (Ann Arbor, Michigan), Order No. 61-5050, 148 pp., Dissertation Abstract, Vol. 22, 1962, pp. 3399-3400.

## PART I

A previous investigation<sup>1</sup> has suggested that chronopotentiometric quarter-wave potentials,  $E_{1/4}$ , obtained for the oxidation of a limited number of substituted ferrocenes can be correlated with the appropriate summation of the Taft substituent constant,  $\Sigma\sigma^*$ . Many additional mono- and di-substituted ferrocenes, covering a wide range of steric, resonance, and inductive effects, have now been oxidized at a platinum foil electrode in lithium perchlorate-acetonitrile medium. A plot of  $E_{1/4}$  versus

$\Sigma\sigma^*$  for these compounds shows a definite linear relationship. The equation of the regression line is

$$E_{1/4} = 0.0978 \Sigma\sigma^* - 0.1374$$

with a correlation coefficient of 0.977. On the basis of this plot, the  $E_{1/4}$  values of certain substituents are more anodic than expected. Interaction of the substituents with the  $h a_g$  molecular orbital of the ferrocene nucleus is the most likely explanation for this behavior.

An equally good correlation is obtained for a similar plot of  $E_{1/4}$  versus  $\Sigma\sigma_p$ . The equation of the regression line for this relationship is

$$E_{1/4} = 0.431 \Sigma\sigma_p + 0.367$$

with a correlation of 0.979. Moreover, this relationship takes into account the substituents which are not successfully correlated by the  $\Sigma\sigma^*$  substituent constants. Because of this fact, the relationship of  $E_{1/4}$  and  $\Sigma\sigma_p$  is favored as best describing the effects of substituents in the oxidation of ferrocenes.

$E_{1/4}$  values for para-substituted phenylferrocenes show excellent correlation with the Hammett substituent constants,  $\sigma_p$ . This result is in agreement with the work of Mason and Rosenblum,<sup>2</sup> who correlated formal oxidation potentials of arylferrocenes with  $\sigma_p$  for the same series of compounds. The equation of the regression line for the plot of  $E_{1/4}$  versus  $\sigma_p$  is

$$E_{1/4} = 0.132 \sigma_p + 0.361$$

with a correlation of 0.998.

## PART II

It has been shown<sup>3</sup> that the initiation of styrene polymerization can be accomplished by electrons supplied at a cathode. The molecular weight of the polymer thus obtained is dependent on the current density at the cathode. The electrolysis of styrene in pyridine containing 0.5 M sodium iodide between magnesium electrodes under unstirred conditions has been carried out at various current densities. The data obtained show the existence of a trend toward lower molecular weight polymers on electrolyses at higher current densities.

## REFERENCES

- 1a. T. Kuwana, Ph. D. Thesis, University of Kansas, 1959.
- b. D. E. Publitz, G. Hoh, and T. Kuwana, Chem. and Ind., 635 (1959).
- c. T. Kuwana, D. E. Publitz, and G. Hoh, J. Am. Chem. Soc., 5811 (1960).
2. J. G. Mason and M. Rosenblum, *ibid.*, 82, 4206 (1960).
3. J. Y. Yang, W. E. McEwen, and J. Kleinberg, *ibid.*, 79, 5833 (1957).
47. Kuwana, T., Publitz, D. E., and Hoh, G. L. K.,  
CHRONOPOTENTIOMETRIC STUDIES ON THE OXIDATION OF  
FERROCENE, RUTHENOCENE, OSMOCENE, AND SOME OF  
THEIR DERIVATIVES, American Chemical Society Journal,  
Vol. 82, No. 22, 1960, pp. 5811-5817.

Oxidation-reduction potentials obtained by a chronopotentiometric method at a Pt electrode in acetonitrile solution indicated that electron-withdrawing substituents decrease the ease of oxidation, while electron-donating substituents increase the ease of oxidation with respect to the parent metallocenes. This agrees with results normally expected from inductive effects. The  $E_{1/4}$  values of ferrocene, osmocene, and ruthenocene are +0.31, +0.63, and +0.69 v. versus S. C. E., respectively. The  $E_{1/4}$  values of ferrocene and its derivatives were correlated with the substituent constructions of the Ingold-Taft equation. Ruthenocene undergoes a 1-step, 2-electron oxidation, and osmocene undergoes a 2-step, 1-electron each, oxidation. Ferrocene shows only a 1-electron transfer. The electrode reaction of ferrocene is nearly reversible, while those of ruthenocene and osmocene show irreversible characteristics.

48. Little, W. F., Reilley, C. N., Johnson, J. D., Lynn, K. N., and Sanders, A. P.,

CHRONOPOTENTIOMETRIC STUDIES OF FERROCENE DERIVATIVES. I. DETERMINATION OF SUBSTITUENT CONSTANTS WITH SUBSTITUTED PHENYLFERROCENES. II. DIRECTLY SUBSTITUTED FERROCENES, American Chemical Society Journal, Vol. 86, No. 7, 1964, pp. 1376-1386.

## I

Chronopotentiometric quarter-wave potentials were measured for a series of 49 o-, m-, and p-substituted phenylferrocenes. With the twelve m- and p-derivatives whose primary substituent constructions were known, the regression line was established:  $\Delta E_{1/4} = 0.128 \sigma + 0.024 \text{ v.}$ , and from this line secondary  $\sigma$ -constructions were obtained for fifteen groups. Similarly,  $\Delta E_{1/4}$  for nine o-substituted phenylferrocenes was correlated with Taft's o-substituent constructions and several new secondary o-constructions were determined from the line of regression:  $\Delta E_{1/4} = 0.126 \sigma_o^* + 0.031 \text{ v.}$  From the potentials of nine p-ferrocenylazobenzenes the transmission of electronic effects through the phenylazo system was studied and the ratio  $\rho_{XC_6H_4N_2} / \rho_X$  was determined to be 0.13, which is in good agreement with previously obtained values.

## II

Chronopotentiometric quarter-wave potentials of mono-substituted ferrocenes were correlated with Hammett para  $\sigma$ -constructions, according to the equation:  $\Delta E_{1/4} = 0.450 \sigma_p + 0.022 \text{ v.}$  Secondary para  $\sigma$ -constructions were derived from quarter-wave potentials of additional derivatives. This same regression line was used to correlate data on 21 heteroannular disubstituted ferrocenes. Correlations with  $\Sigma\sigma^*$  and  $\Sigma\sigma_1$  are discussed.

49. Nefedova, M. N., Kursanov, D. N., Perevalova, E. G., Setkina, V. N., and Nesmeyanov, A. N.,

SUBSTITUENT EFFECT ON THE RATE OF ISOTOPIC HYDROGEN EXCHANGE IN FERROCENE DERIVATIVES, Doklady Akademii Nauk SSSR, Vol. 166, No. 2, 1966, pp. 374-377 (In Russian).

The D-H exchange of substituted ferrocenes was studied in  $CF_3CO_2D$  with AcOH or  $CH_2Cl_2$  diluents, at 25° under N



atmosphere. For monosubstituted ferrocenes the following relative rates were found: Me 10.7, Et 10.7, MeO 6.7, Ph 0.6, Cl 0.025, and CO<sub>2</sub>Me 0.01; for 1,1'-disubstituted ferrocenes: Et 50.8, MeO 23.3, Ph 0.33 and Cl 0.0007. The results indicated the effect of both the inductive and the resonance effects of the substituent groups.

50. Perevalova, E. G., Gubin, S. P., Smirnova, S. A., and Nesmeyanov, A. N.,  
OXIDATION-REDUCTION POTENTIALS OF HETEROANNU-  
LARLY DISUBSTITUTED FERROCENES, Doklady Akademii  
Nauk SSSR, Vol. 155, No. 4, 1964, pp. 857-860.

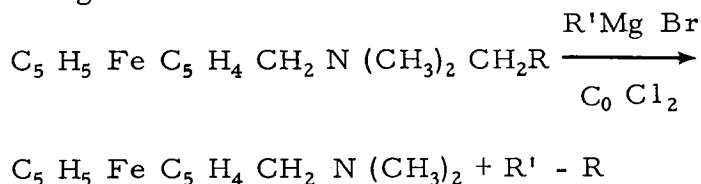
The effect of substituents on oxidation-reduction potentials of ferrocenes with two substituents in different rings were additive. The following values were determined (CA 57, 9575c) (substituents shown): Et, Et, -0.150 v.; Et, Br, -0.357; CH<sub>2</sub>OH, CH<sub>2</sub>CH, -0.386; AcO, AcO, -0.387; Et, CONH<sub>2</sub>, -0.422; Bu, CO<sub>2</sub>H, -0.451; Pr, CO<sub>2</sub>H, -0.453; Et, CO<sub>2</sub>H, -0.455; I, Cl, -0.529; Cl, Cl, -0.554; and MeO, CO<sub>2</sub>H, -0.410.

51. Perevalova, E. G., Gubin, S. P., Smirnova, S. A., and Nesmeyanov, A. N.,  
OXIDATION-REDUCTION PROPERTIES OF COMPOUNDS  
WITH TWO FERROCENYL GROUPS, Doklady Akademii  
Nauk SSSR, Vol. 147, 1962, pp. 384-387.

Titration curves are shown for ferrocene, Me ferrocenecarboxylate, m-nitrophenylferrocene, methoxyferrocene, diferrocenyl, diferrocenylmercury, and diferrocenylmethane, titrated in AcOHHClO<sub>4</sub> solution by means of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>. The following oxidation-reduction potentials were determined for diferrocenyl compounds. (bridge group between ferrocene nuclei shown): Hg, -0.283 and -0.655 v.; CH<sub>2</sub>, -0.189 and -0.308; CH<sub>2</sub>CH<sub>2</sub>, -0.214 and -0.282; CH<sub>2</sub>OCH<sub>2</sub>, -0.266 and -0.325; and CH<sub>2</sub>NMe<sub>2</sub>CH<sub>2</sub>, -0.189. The following values were determined for monosubstituted ferrocenes: Me, -0.199; Et, -0.201; H, -0.198; CO<sub>2</sub>H, -0.272; NHBz, -0.302; PhCH<sub>2</sub>O, -0.302; MeO, -0.302; HO, -0.309; NHMe<sub>2</sub><sup>+</sup>, -0.443; and NMe<sub>2</sub>Et<sup>+</sup>, -0.479. A good agreement with the Taft inductive constants for the substituents was observed.

52. Perevalova, E. G. and Ustynyuk, Y. A.,  
 REACTIVITY OF COMPOUNDS CONTAINING THE FERRO-  
 CENYLMETHYL GROUP. COMMUNICATION 3. REACTIONS  
 OF QUATERNARY AMMONIUM COMPOUNDS CONTAINING  
 A FERROCENYLMETHYL GROUP WITH ORGANOMAGNE-  
 SIUM COMPOUNDS IN PRESENCE OF COBALT CHLORIDE,  
 Translated from Izvestiya Akademii Nauk SSSR, Seriya  
Khimicheskaya, No. 10, October 1963, pp. 1776-1782.

The reaction of ammonium salts of the general formula  $[C_5H_5FeC_5H_4CH_2N^+(CH_3)_2CH_2R]X^-$ , in which  $CH_2R =$  propyl, allyl, benzyl, and ferrocenylmethyl, with Grignard reagents in the presence of anhydrous cobalt chloride were studied. The results show that the ferrocenyl nucleus stabilizes a neighboring radical center to a smaller extent than a benzene nucleus does. In general the reaction proceeds according to:



53. Perevalova, E. G., Ustynyuk, Y. A., and Nesmeyanov, A. N.,  
 REACTIVITY OF COMPOUNDS CONTAINING THE FERRO-  
 CENYLMETHYL GROUP. COMMUNICATION 2. EMDE  
 SODIUM AMALGAM REDUCTION OF QUATERNARY AMMO-  
 NIUM SALTS CONTAINING THE FERROCENYLMETHYL  
 GROUP, Translated from Izvestiya Akademii Nauk SSSR,  
Ordelenie Khimicheskikh Nauk, No. 6, June 1963, pp. 1045-  
 1049.

The Emde sodium amalgam reduction of quaternary ammonium salts,  $[C_5H_5FeC_5H_4CH_2N^+(CH_3)_2CH_2R]X^-$  where  $R =$  methyl, allyl, and benzyl, was studied in order to assess the stabilizing action of the ferrocene system on the adjacent radical center and compare the stability of the ferrocenylmethyl radical with those of the allyl and benzyl radicals. The results show a ferrocene nucleus stabilizes a neighboring radical center to a lesser extent than benzene, to a greater extent than a methyl, and about the same extent as an allyl group.

54. Purdue University, Lafayette, Indiana,  
CHEMISTRY OF FERROCENE AND RELATED COMPOUNDS,  
FINAL REPORT by Robert A. Benkeser, January 1963,  
AD-600-969, N64-32822, Contract No. AF-49 (638)-297  
(Unclassified Report).

There were four primary objectives in this research project:

- 1) A series of ferrocene compounds containing a carboxyl group in one of the rings and a variety of other electron supplying and withdrawing groups in the other ring were synthesized.
- 2) Free radical addition reactions to the vinylferrocene group in view of obtaining new types of ferrocene compounds were studied and demonstrated by equations.
- 3) Methods of decomposing substituted ferrocenes into their present cyclopentadienes with the principal purpose of working out a method for identifying new ferrocene structures were discussed.
- 4) A study was made of the metalation of various alkylferrocenes with n-amylsodium. A competitive metalation between ferrocene and benzene was carried out with a limited amount of n-amylsodium.

55. Rosenblum, M., Santer, J. O., and Howells, W. G.,  
THE STRUCTURE AND CHEMISTRY OF FERROCENE. VIII.  
INTERANNULAR RESONANCE AND THE MECHANISM OF  
ELECTROPHILIC SUBSTITUTION, American Chemical  
Society Journal, Vol. 85, 1963, pp. 1450-1458 (cf. CA 58,  
1023a).

Certain anomalous features of Friedel-Crafts acetylation reactions involving ferrocene are shown to be due to protonation of the metal atom. The relative rates of acetylation of ferrocene and acetylferrocene, compared with an assigned rate of 1.0 for benzene, were found to be  $3.3 \times 10^6$  and  $1.9 \times 10^2$ , respectively. The large interannular deactivation owing to the acyl function cannot be accounted for in terms of inductive or direct electrostatic field effects. While these results imply effective interannular electronic transmission, the ultraviolet absorption spectra of a number of arylferrocenes fail to reveal any pronounced coupling of heteroannularly disposed groups. These apparently conflicting findings are

reconciled in terms of a general mechanism for electrophilic substitution in which the metal atom is the primary site for electrophilic attack. The energetics and stereochemistry of these reactions and the comparative reactivities of the iron group metallocenes are considered. Certain broader implications of this theory are discussed.

56. Schlogel, K. and Fried, M.,  
OPTICALLY ACTIVE HYDROCARBONS OF THE FERROCENE  
SERIES, Tetrahedron Letters, No. 22, 1963, pp. 1473-1478  
(in German).

Refer to item No. 14 for abstract.

57. Tirouflet, J., Laviron, E., Dabard, R., and Komenda, J.,  
STUDIES IN METALLOCENE SERIES. II. POLAROGRAPHIC  
AND OSCILLOGRAPHIC INVESTIGATION OF THE EQUILIB-  
RIUM METALLOCENIUM. STRUCTURAL EFFECTS, Societe  
Chimique de France. Bulletin, 1963, pp. 857-862 (cf. CA 57,  
3482h).

Reversibility of the system ferrocene -  $e \rightleftharpoons$  ferricinium ion was proved by using  $dE/dt$  versus  $E$  curves, single sweep method, and controlled-potential electrolysis with Pt rotating electrode as indicator electrode. Identity of  $(E_{1/2})_{Ox}$  and  $(E_{1/2})_{Red}$  was proved also by using  $HNO_3$  oxidation for ferrocene (I) and for the oxidized and reduced form at the Hg electrode of osmocene (II) and nickelocene (III). For anodic waves the following values of  $E_{1/2}$  were measured (in 0.5N  $HClO_4$  in 50 percent EtOH): I + 0.19; II - 0.07; III - 0.18 v. For substituted I, the following values of  $E_{1/2}$  measured with rotating Pt electrode were obtained (substituent given):  $NH_2$  +0.02;  $AcNH$  +0.18;  $H$  +0.20;  $C (Me)$ :  $NOH$  +0.40;  $\alpha-CH$ :  $NOH$  +0.42;  $\beta-CH$ :  $NOH$  +0.43;  $C (Me)$ :  $-NNHCONH_2$  +0.50;  $CH:NNHCONH_2$  +0.51;  $CHO$  +0.51;  $Ac$  +0.51,  $CH_2OH$  +0.20,  $COOH$  +0.42;  $Ac_2$  +0.84;  $Ph$  +0.2; and iodine +0.33 v. Values of half-wave potentials and potentials of indentations on  $dE/dt$  versus  $E$  curves were correlated by using the Hammett equation and  $\sigma_p$  values.

58. Aerospace Corporation, Los Angeles, California,  
COMPLEX TRANSITION METAL HYDRIDES by S. G. Gibbins,  
November 1963, Report No. TDR-269-4210-10-1, SSD-TDR-  
63-283, AD-425 588, Contract No. AF04 695 269 (Unclassified  
Report)

A review of the properties of complex transition metal hydrides and a discussion of the probable mechanism requisite for stability are given. The absence of stoichiometric binary transition metal hydrides coupled with features common to the complex ones indicates that the primary stabilization mechanism of the transition metalhydrogen bond is one involving multiple bonding between the metal and the stabilizing ligand. The multiple bond comprises of a sigma bond, the electron pair being provided by the ligand, and a pi bond, the electron pair being provided by the metal. Thus, negative charge that would have accumulated on the metal, if only a sigma bond existed, is diminished. From a molecular orbital point of view, the pi bond permits formerly-metal non-bonding D orbitals to become bonding. Thus, the total energy of the system is reduced and the stability is increased.

59. Bailey, R. T. and Lippincott, E. R.,  
THE VIBRATIONAL SPECTRUM OF DIMETHYLFERROCENE,  
Spectrochimica Acta, Vol. 21, No. 3, 1965, pp. 389-398

The infrared (4000-250  $\text{cm}^{-1}$ ) and Raman (up to 1650  $\text{cm}^{-1}$ ) spectra of dimethylferrocene are reported. The Raman spectrum was excited by a radio-frequency-powered Rb plasma arc. The spectra were consistent with a model involving little interaction between the methylcyclopentadienyl rings and having pseudo  $C_{2v}$  symmetry. A reasonable assignment of the fundamental vibrations, based on this model, was made by comparison with ferrocene and toluene and utilizing the inequality rule proposed by Steele and Whiffen (CA 54, 2008i). The assignment was also consistent with the modified product rule due to Pitzer and Scott (CA 37, 4297<sup>5</sup>).

60. Benkeser, R. A., Nagai, Y., and Hooz, J.,  
 IMPORTANCE OF NUCLEAR MAGNETIC RESONANCE  
 (N. M. R.) IN DETERMINING STRUCTURE AND ELECTRICAL  
 EFFECTS IN SUBSTITUTED FERROCENES, Chemical  
Society of Japan Bulletin, Vol. 36, 1963, pp. 482-483.

N. M. R.  $\tau$  values for the ring protons of substituted ferrocenes were determined as an aid to structural analysis. Thus, ring values obtained on a spectrometer by using  $\text{Si}(\text{Me})_4$  as an internal reference were (substituents given, with chemical shifts listed as a = 11 in 2- and 5-position relative to the acetyl group, b = 11 in 3- and 4-position relative to acetyl group, c = 11 on unsubstituted ring, d = 11 on alkylated ring, with relative intensities given in parentheses): 11, e = 5.94; d = Me, e = 6.01 (7), d = 26.06 (2); Et, c = 5.99 (5), 6.03, d = 6.03 (4); i-Pr, c = 5.98 (5), d = 6.04 (4); tert-Bu, c = 5.98 (5), d = 6.08 (4); Ac, a = 5.33 (2), b = 5.64 (2), c = 5.88 (5); 1-Ac-1'-Me, a = 5.42 (2), b = 5.70 (2), d = 6.01 (4); 1-Ac-2-Me, a = 5.56 (1), b = 5.72 (1), 5.82 (1), c = 5.95 (5); 1-Ac-3-Me, a = 5.40 (2), b = 5.69 (1), c = 5.92 (5); 1-Ac-1'-Et, a = 5.41 (2), b = 5.69 (2), d = 5.99 (4); 1-Ac-2-Et, a = 5.53 (1), b = 5.69 (1), 5.79 (1), c = 5.93 (5); 1-Ac-3-Et, a = 5.37 (2), b = 5.69 (1), c = 5.91 (5); 1-Ac-1'-i-Pr, a = 5.39 (2), b = 5.66 (2), d = 5.98 (4); 1-Ac-2-i-Pr, a = 5.51 (1), b = 5.64 (1), 5.76 (1), c = 5.92 (5); 1-Ac-3-i-Pr, a = 5.41 (2), b = 5.71 (1), c = 5.91 (5); 1-Ac-1'-tert-Bu, a = 5.32 (2), b = 5.61 (2), d = 5.98 (4); 1-Ac-2-t-Bu, a = 5.46 (1), b = 5.71 (1), 5.79 (1), c = 5.85 (5); and 1-Ac-3-tert-Bu, a = 5.43 (2), b = 5.72 (1), c = 5.90 (5). Values for  $\alpha$ -protons on the alkyl groups were (R = indicated group): Me, 8.04; Et, 7.71; iso-Pr, 7.41; for 1-Ac-1'-R: Me 8.09, Et, 7.73, iso-Pr, 7.41; for 1-Ac-2-R, Me, 7.67, Et, 7.28, iso-Pr 6.59; and for 1-Ac-3-R: Me 7.97, Et 7.62, iso-Pr 7.34.

61. Bohn, R. K. and Haaland, A.,  
 ON THE MOLECULAR STRUCTURE OF FERROCENE,  
 $\text{Fe}(\text{C}_5\text{H}_5)_2$ , Journal of Organometallic Chemistry, Vol. 5,  
 No. 5, 1966, pp. 470-476,

Electron diffraction studies of ferrocene vapor at  $140^\circ$  show that the free molecule has an eclipsed ( $\text{D}_{5h}$ ) equilibrium configuration with a small barrier to internal rotation. The barrier is estimated to be about 1.1 kcal./mole. The principal molecular parameters are: C-C,  $1.431 \pm 0.005$  A.; Fe-C,

2.058  $\pm$  0.005 Å., and C-H 1.122  $\pm$  0.020 Å. The C-H bonds seem to be bent about 5 ° out of the plane of the C<sub>5</sub> ring towards the iron atom.

62. California University, Los Angeles, California,  
STUDY OF ORGANIC COMPOUNDS OF UNUSUAL GEOMETRY  
OR ELECTRONIC STRUCTURE, FINAL REPORT, JANUARY-  
DECEMBER 1963 by K. N. Trueblood, April 1964, Report No.  
AFOSR-64-1107, AD-601 478, Contract No. AF AFOSR240 63  
(Unclassified Report).

The report includes further development of applications of high-speed computers in crystallographic structure work. A description is given of a precise study of the structure of tetracyanoquinodimethane, heteroaromatic dibenzo-1, 3A, 4, 6A-tetraazapentalene, an aminotroponeimine derivative with aromatic properties, and a ferrocene derivative in which the two cyclopentadienyl rings are joined by a two-carbon bridge. Preliminary reports are given of reinvestigations of the structures of tetracyanoethylene and di-p-zylylene. A description of the structure of the hydrated calcium salt of the unusual acid hexacyanoisobutylene. The anion of this acid is highly stabilized by resonance, and preliminary considerations might suggest that it should be planar; in fact, however, we find it to be propeller-shaped, with the arms tilted about 24 degrees. This tilt does not reduce the pi-overlap very much and does relieve intramolecular steric strain considerably.

63. California University, Department of Chemistry, Los Angeles, California,  
THE CRYSTAL AND MOLECULAR STRUCTURE OF 1, 1'-  
TETRAMETHYLETHYLENEFERROCENE by M. B. Laing  
and K. N. Trueblood, August 1964, Report No. AFOSR-65-  
2387, AD-627 955, Contract No. AF49 (638)-719 (Unclassified  
Report) (Acta Crystallographica, Vol. 19, pt. 3, September  
1965, pp. 373-381).

1, 1'-tetramethylethyleneferrocene forms monoclinic plates of space group P2<sub>1</sub>/C, and four molecules in the unit cell with A = 7.756, B = 10.97, C = 15.41, and beta = 92.63 degrees. The structure was solved from three-dimensional Patterson and Fourier syntheses, and was refined by block-diagonal least squares.

The two five-membered rings are tilted 23 degrees with respect to one another, but because of the bridge linking them are staggered only by about 9 degrees, in contrast to ferrocene. The strain in the molecule is apparent also in the fact that the dihedral angles in the bridge are only about 26 degrees, and that the exocyclic bonds are bent about 11 degrees from the ring planes. The bond distances in the bridge are slightly greater than normal. The bond distances in the ring and to the iron atom appear normal.

64. Dvoryantseva, G. G., Sheinker, Y. N., Yur'eva, L. P., and Nesmeyanov, A. N.,  
STRUCTURE ESTABLISHMENT OF SOME ISOMERIC  
DISUBSTITUTED FERROCENES FROM THEIR INFRARED  
ABSORPTION SPECTRA, Doklady Akademii Nauk SSSR, Vol.  
156, No. 4, 1964, pp. 873-876.

On the basis of previous reports by Rosenblum et al. (R., CA 54, 4528d; R., et al., CA 57, 15149b), on spectra of ferrocene derivatives and the observed infrared bands in 910-20 and 930-50  $\text{cm}^{-1}$  regions, as well as 880-90 and 950-70  $\text{cm}^{-1}$  regions, the following assignments of orientation of groups are made: 1, 1'- $\text{MeC}_5\text{H}_4\text{FeC}_5\text{H}_4\text{CONH}_2$ , m. 145-6°; 1, 1'- $\text{EtC}_5\text{H}_4\text{FeC}_5\text{H}_4\text{CONH}_2$ , m. 141-2°; 1, 1'- $\text{PhC}_5\text{H}_4\text{FeC}_5\text{H}_4\text{CONH}_2$ , m. 127-8°; 1, 1'- $\text{MeC}_5\text{H}_4\text{FeC}_5\text{H}_4\text{CN}$ , m. 72-3°; 1, 1'- $\text{EtC}_5\text{H}_4\text{FeC}_5\text{H}_4\text{CN}$ , m. 29-30°; 1, 2-Me ( $\text{H}_2\text{NCO}$ )  $\text{C}_6\text{H}_3\text{FeC}_5\text{H}_5$ , m. 119-20°; 1, 2-Et ( $\text{H}_2\text{NCO}$ )  $\text{C}_5\text{H}_3\text{FeC}_6\text{H}_5$ , m. 95-6°; 1, 2-Me (NC)  $\text{C}_5\text{H}_3\text{FeC}_5\text{H}_5$ , m. 51-2°; 1, 2-Et (NC)  $\text{C}_5\text{H}_3\text{FeC}_5\text{H}_5$ , an oil; 1, 3-Me ( $\text{H}_2\text{NCO}$ )  $\text{C}_5\text{H}_3\text{FeC}_6\text{H}_5$ , m. 146-7°; 1, 3-Et ( $\text{H}_2\text{NCO}$ )  $\text{C}_5\text{H}_3\text{FeC}_5\text{H}_5$ , m. 161-2°; 1, 3-Me (NC)  $\text{C}_6\text{H}_3\text{FeC}_5\text{H}_5$ , m. 45-6°; 1, 3-Et (NC)  $\text{C}_5\text{H}_3\text{FeC}_5\text{H}_5$ , an oil; Ph ( $\text{H}_2\text{NCO}$ )  $\text{C}_5\text{H}_3\text{FeC}_5\text{H}_5$ , m. 219-20°; Ph ( $\text{H}_2\text{NCO}$ )  $\text{C}_5\text{H}_3\text{FeC}_5\text{H}_5$  (the last 2 substances were probably 1, 3- and 1, 2-isomers, respectively).

65. Fischer, R. D.,  
THE METAL-RING BONDING IN SANDWICH COMPLEXES,  
Theoretica Chimica Acta, Vol. 1, 1963, p. 418.

The application of the simple LCAO-MO-approach of Wolfsberg and Helmholz on sandwich-complexes leads for ferrocene and dibenzenechromium to remarkable agreements with SCF-calculations of Shustorovich and Dyatkina as far as bonding MO's are concerned.



The overlap integrals obtained for complexes of the type  $(C_nH_n)_2 Me$  ( $n = 4 - 8$ ) from simplified SCF wave functions turn out to present fairly favorable overlap conditions even for  $n = 7$  and  $8$ .

The participation of f-orbitals which should in principle be possible in the bonds of the hypothetical complex  $(C_8H_8)_2 U$  is discussed.

66. German, E. D. and Dyatkina, M. E.,  
CALCULATION OF G-FACTORS OF AROMATIC COMPLEXES  
OF METALS BY THE MOLECULAR ORBITAL METHOD,  
Journal of Structural Chemistry, Vol. 6, No. 6, 1965,  
pp. 898-903 (in Russian).

The g-factors of aromatic complexes of metals were calculated by the molecular orbital method on the assumption that the unpaired electrons are in molecular orbitals including both orbitals of the metal and of the ligands. Calculations for  $Cr(C_6H_6)_2^+$ , the ground state of which is an orbital singlet, yielded the following results: theoretical values of  $g$ ,  $g$ , and  $(g)$  1.986, 2.0023, and 1.989, respectively, and  $(g)$  (experimental) 1.984. The theoretical value of  $(g)$  agreed with the experimental determined value reported by Voevodskii, et al. (*Optika i Spektroskopiya*, Vol. 5, No. 1, 1958, pp. 90-92. Calculations for  $Fe(C_5H_5)_2^+$ ,  $Ti(C_5H_5)_2^+$ , and  $V(C_5H_5)_2^{2+}$ , the ground state of which is an orbital doublet, were carried out without consideration of the Jahn-Teller effect (A) and with consideration of this effect (B). Because the molecular orbital coefficients and the energies of vanadiocene and titanocene are not known, approximate values for the g-factors of these compounds were obtained. Values A did not agree with those determined experimentally (Noeth et al., CA 54, 14961f). values B, calculated on the assumption that degeneration was removed by the Jahn-Teller effect, and that this effect must be considered together with spin-orbital interaction, showed better agreement with experimentally determined values. On the basis of the \*

	A			B			(g)
	g	g	(g)	g	g	(g)	exptl.
$Fe(C_5H_5)_2^+$	0	6.045	3.45	1.987	2.246	2.070	2.014
$Ti(C_5H_5)_2^+$	0	~2.0023	~1.16			<2.0023	1.975
$V(C_5H_5)_2^{2+}$	0	~2.0023	~1.16			<2.0023	1.937

results obtained, the assumption of Robertson and McConnell (CA 54, 11704g) that orbital degeneration is split by spin-orbital interaction in  $V(C_5H_5)_2^{2+}$ ,  $Ti(C_5H_5)_2^+$ , and  $Fe(C_5H_5)_2^+$  to such an extent that the Jahn-Teller effect is not exhibited seems to be unjustified.

67. Kaluski, Z. L. and Struchkov, Y. T.,  
THE CRYSTAL AND MOLECULAR STRUCTURE OF  
DICHLORODIFERROCENYL, Journal of Structural Chemistry,  
Vol. 6, No. 5, 1965, pp. 745-754 (in Russian) (cf. CA 63,  
10794h).

As found by x-ray analysis, bis [1- (2'-chloroferrocenyl)] has a monoclinic structure, with a 10.63, b 8.65, and c 10.60 Å.,  $\beta$  121.5°; d. (experimental) is 1.68, Z = 2, and the space group  $P2_1/c$ , with the molecules in the prismatic trans conformation. Mean bond lengths are: Fe-C 2.07, C-C (within rings) 1.46, C-C (between rings) 1.51, and C-Cl 1.76 Å. The angle between the planes of the rings in the ferrocene sandwich is 4° and the C-C distance between the rings is 3.30 Å.

68. Kaluski, Z. L., Struchkov, Y. T., and Avoyan, R. L.,  
X-RAY STUDY OF THE DIFERROCENYL STRUCTURE,  
Journal of Structural Chemistry, Vol. 5, 1964, p. 683.

A complete x-ray study of the structure of diferrocenyl, the crystals of which belong to the  $P2_1/c$  group of the monoclinic symmetry class (a = 10.17, b = 7.86, c = 12.62 Å,  $\beta$  = 132°, N = 2), was carried out by calculating a three-dimensional series expansion of the electron density and applying the method of least-square fitting. The molecule occupies the special position at the symmetry center, i. e., has the trans configuration with respect to the  $C_1 - C_1$  bond between the ferrocene groups. The bond lengths (Fe - C =  $2.03_5 \pm 0.02$ , C - C =  $1.42 \pm 0.04$  Å) and the valence angles (C - C - C =  $108 \pm 2.5^\circ$ ) are identical to those found in ferrocene itself. The length of the  $C_1 - C_1$  bond between the ferrocene groups, equaling 1.48 Å, is slightly reduced, which points to distinct conjugation between these groups in the molecule. It is interesting that the angle  $\varphi$  = 16° through which one cyclopentadiene ring in the sandwich has been turned with respect to the other is intermediate between the values corresponding to the proper prismatic ( $\varphi$  = 0°) and antiprismatic ( $\varphi$  = 36°) configurations.

69. MacDonald, A. C. and Trotter, J.,  
THE CRYSTAL AND MOLECULAR STRUCTURE OF  
BIFERROCENYL, Acta Crystallographica, Vol. 17, 1964,  
p. 872.

Crystals of biferrocenyl,  $C_5H_5 \cdot Fe \cdot C_5H_4 \cdot C_5H_4 \cdot Fe \cdot C_5H_5$ , are monoclinic, with  $a = 10.35$ ,  $b = 7.87$ ,  $c = 12.63$  Å,  $\beta = 131.72^\circ$ . The space group is  $P2_1/c$  and there are two molecules in the unit cell, so that a molecular centre of symmetry is required. The intensities of 1111 reflexions were measured with a scintillation counter, MoK $\alpha$  radiation being used. The structure was determined by Patterson and Fourier methods, and refined by least squares and differential syntheses. The final R value for 896 observed reflexions is 0.16.

Each iron atom is sandwiched between two five-membered rings which are planar, approximately parallel, separated by 3.32 Å, and oriented about midway between the fully eclipsed and fully staggered conformations. The two five-membered rings which are bonded together are coplanar, and the molecular configuration is trans. The mean bond distances are Fe - C = 2.04 Å, C - C (in cyclopentadienyl rings) = 1.40 Å, C - C (between rings) = 1.48 Å. There are however deviations from fivefold symmetry which are possibly significant; these deviations are the same in both crystallographically independent rings, and are similar to those observed (but considered not significant) in ferrocene. All the intermolecular separations correspond to normal van der Waals interactions.

70. Mark, V. and Rausch, M. D.,  
DIVERGENCE IN THE RELATIVE SHIELDING OF RING AND  
SIDE-CHAIN PROTONS IN SUBSTITUTED METALLOCENES,  
Inorganic Chemistry, Vol. 3, No. 7, 1964, pp. 1067-1069.

Reduction of the acetyl- or benzoyl-metallocene with  $LiAlH_4-AlCl_3$  in  $Et_2O$  (CA 55, 1562e) gave ethylruthenocene, ethylosmocene, benzylruthenocene, and benzylosmocene. The nuclear magnetic resonance spectra of these compounds show a gradual deshielding of the ring protons on going from Fe to Ru to Os. The significance of these findings is discussed. (cf. CA 60, 3639g).

71. Mulay, L. N. and Withstandley, V.,  
MAGNETIC SUSCEPTIBILITY ANISOTROPY STUDIES ON  
OSMOCENE: CORRELATION OF  $\pi$ -ELECTRON RING  
CURRENTS WITH CHEMICAL SHIFTS AND BONDING IN  
METALLOCEENES, Journal of Chemical Physics, Vol. 43,  
No. 12, 1965, pp. 4522-4523.

The magnetic susceptibilities, crystal anisotropies, and molecular susceptibility constructions ( $K_1$ ,  $K_2$ , and  $K_3$ ) were measured for osmocene crystals. The number of  $\pi$ -electrons ( $n$ ) in each of the cyclopentadienyl rings was calculated at 2.6 from the values of  $K_1$ ,  $K_2$ , and  $K_3$ . Thus  $n$  decreases successively for each of the compounds ferrocene, ruthenocene, and osmocene. This decrease is caused by a shielding effect at the ring protons which counteracts any deshielding effects due to ring currents. Shielding may be due to either an overlap of the metal and ring orbitals, or to the diamagnetism associated with the 5d shell of Os.

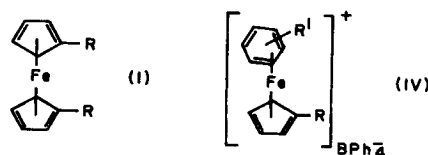
72. Nagai, Y., Hooz, J., and Benkeser, R. A.,  
USE OF NUCLEAR MAGNETIC RESONANCE SPECTRO-  
SCOPY AS A STRUCTURAL PROBE IN FERROCENE  
CHEMISTRY, Chemical Society of Japan Bulletin, Vol. 37,  
No. 1, 1964, pp. 53-60.

A number of acetylalkylferrocenes were prepared and their infrared and nuclear magnetic resonance spectra determined. Results were tabulated. NMR spectra were particularly useful in distinguishing between 1, 2- and 1, 3-disubstituted structures. A series of shielding constructions for a variety of ferrocene substituents was developed and from them the chemical shifts of the protons bonded to the ferrocene nucleus could be accurately predicted for a number of substituents.

73. Nesmeyanov, A. N., Vol'kenau, N. A., and Bolesova, I. N.,  
INTERACTION OF FERROCENE AND ITS DERIVATIVES  
WITH AROMATIC COMPOUNDS, Tetrahedron Letters, No. 25,  
1963, pp. 1725-1729 (cf. CA 59, 6438c).

Ferrocene (I, R = H) (II) heated with aromatic hydrocarbons at 80-165° in the presence of 2- or 4-fold excess of  $AlCl_3$  and an equimolar amount of Al powder yielded the

complex salt from which the arenecyclopentadienyliron cation (III) could be isolated in the form of the tetraphenylborate (IV). Use of Al powder prevented oxidation of II to the ferricinium ion. Only one cyclopentadienyl ring in II was replaced.



The procedure gave 30-66 percent yields of IV ( $R = R' = H$ ) (V),  $C_{35}H_{31}BFe$ , m.  $250-1^\circ$  (decomposition) (compounds were melted in fused capillaries on a block preheated to  $30-40^\circ$  below the m. p.); IV ( $R = H$ ,  $R' = 1, 3, 5\text{-Me}_3$ ) (VI),  $C_{38}H_{37}BFe$ , m.  $257-8^\circ$  (decomposition). IV ( $R = H$ ,  $R' = (CH_2)_4$ ) (VII),  $C_{39}H_{37}BFe$ , m.  $237.5-8.5^\circ$  (decomposition). VI oxidized with  $KMnO_4$  gave trimesic acid, showing the presence of 1, 3, 5- $Me_3C_6H_3$  in a  $\pi$ -complex molecule. VI and VII cations were obtained previously by interaction of  $[C_5H_5Fe(CO)_2]Cl$  with  $C_6H_6$  and 1, 3, 5- $Me_3C_6H_3$ , respectively. The substituted I ( $R = Et, Ac$ ) similarly reacted with 1, 3, 5- $Me_3C_6H_3$  to give IV ( $R = Et, R' = 1, 3, 5\text{-Me}_3$ ),  $C_{40}H_{41}BFeO$ , m.  $197-8^\circ$  (decomposition). Electron withdrawing substituents make the exchange reaction more difficult and electron repellent substituent groups facilitate the exchange reaction. I ( $R = Ac$ ) is less active and I ( $R = Et$ ) more active than II. Treatment of acetylferrocene with 1, 3, 5- $Me_3C_6H_3$  and  $AlCl_3$  gave mainly acetylcyclopentadienylmesityleneiron whereas the major product from ethylferrocene was cyclopentadienylmesityleneiron. IV were yellow crystal solids, soluble in  $Me_2CO$ ,  $CH_2Cl_2$ ,  $MeCN$ , and  $MeNO_2$ , insoluble in petr. ether,  $C_6H_6$ , and  $Et_2O$ . VIII is a light orange solid, solution in alcohol. IV in the solid state are stable to atmospheric O but are affected by sunlight. The cations III are stable in acids but less stable in alk. media. IV in HCl treated with iodine in the presence of KI gave black polyiodides of indefinite iodine content. Reduction of the polyiodides with  $Na_2SO_3$  or  $Na_2S_2O_4$  in boiling alcohol gave the iodides of III ( $R = R' = H$ ),  $C_{11}H_{11}FeI$  (IX), m.  $230-0-30.5^\circ$ ; III ( $R = H$ ,  $R' = 1, 3, 5\text{-Me}$ ),  $C_{14}H_{14}FeI$ , m.  $220-2^\circ$  (decomposition); III ( $R = H$ ,  $R' = (CH_2)_4$ ),  $C_{15}H_{17}FeI$ , m.  $207-8^\circ$  (decomposition). The iodides are yellow crystalline solids, extremely soluble in  $H_2O$ ,  $MeOH$ ,  $EtOH$ , soluble in  $Me_2CO$ , moderately soluble

in  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ , and highly unstable in light. Partial oxidation of the polyiodide, treatment of the polyiodide with excess KI, or treatment of IX with iodine gave the reddish violet triiodide  $[\text{C}_5\text{H}_5\text{NFeC}_6\text{H}_6][\text{I}_3]$ , m.  $226-7^\circ$  (decomposition). The tetraphenylborates and iodides of III pyrolyzed at  $230-300^\circ$  gave I ( $\text{R} = \text{H}$ ).

74. Princeton University, Plastics Laboratory, New Jersey, STUDIES ON THE ELECTRONIC ACTIVITY OF METAL ATOMS IN METALLOCENE SYSTEMS by D. S. Trifan and R. Bacskai, AD-248 980 (Unclassified Report).

Not abstracted.

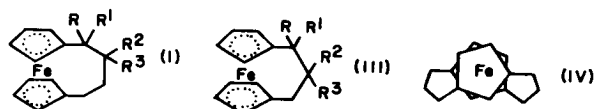
75. Rausch, M. D. and Mark, V., PROTON NUCLEAR MAGNETIC RESONANCE ANALYSIS OF ACYL METALLOCENES, Journal of Organic Chemistry, Vol. 28, No. 11, 1963, pp. 3225-3228 (cf. CA 54, 21025i).

The chemical shifts at ring positions, the multiplicity, and the line separation in the apparent triplets, J, are tabulated for ferrocene, ruthenocene, osmocene, acetylferrocene, acetylruthenocene, acetylosmocene, 1, 1'-diacetylferrocene, 1, 1'-diacetylruthenocene, 1, 1'-diacetylosmocene, benzoylferrocene, benzoylruthenocene, benzoylosmocene, 1, 1'-dibenzoylferrocene, 1, 1'-dibenzoylruthenocene, and 1, 2-dibenzoylruthenocene. The results are discussed. The occurrence of well resolved and well separated lines in the nuclear magnetic resonance spectra of various metallocene derivatives designates these compounds as suitable substrates for the study of substituent effects on the ring protons.

76. Rosenblum, M., Banerjee, A. K., Danieli, N., and Herrick, L. K., STRUCTURE AND CONFORMATION OF BRIDGED FERROCENES, Tetrahedron Letters, 1962, pp. 423-427.

Several singly or doubly bridged ferrocenes were prepared and their nuclear magnetic resonance spectra examined. In 1, 1'-trimethyleneferrocene ( $\text{I}$ ,  $\text{R} = \text{R}^1 = \text{R}^2 = \text{R}^3$ ) ( $\text{II}$ ) a half cyclohexane conformation for the 3 C atom bridge is not possible and geometrical requirements are met by rotation of  $\text{C}_\alpha$  valences about the  $\text{C}_\alpha\text{-C}_\beta$  bond through  $23^\circ 55'$ , resulting

in tilting of the rings by an angle of  $15^{\circ}3'$  from their parallel orientation. These



metal-ring bond deformations do not introduce any detectable magnetic inequivalence in ring protons since these give rise to sharp singlet absorption at  $6.05 \gamma$  in II as in I, 1'-dimethylferrocene. The apparent magnetic equivalence of methylene protons at  $8.05 \tau$  in II is admissible only in terms of a rapid inversion effectually averaging the spatial orientations of the protons. The considerable strain of such a configuration was shown by failure of I ( $RR^1 = O$ ,  $R^2 = R^3 = H$ ) to undergo catalyzed D exchange such as readily undergone by the enol form of the homologous ketone (III,  $RR^1 = O$ ,  $R^2 = R^3 = H$ ). Pyrolysis of I ( $R^1 = R^2 = R^3 = H$ ,  $R = OAc$ ,  $OBz$ ,  $p-O_2NC_6H_4CO_2$ ,  $MeOCO_2$  and  $EtOCO_2$ ) gave no detectable amount of olefin but the latter reactions gave I ( $R^1 = R^2 = R^3 = H$ ,  $R = OMe$ ,  $OEt$ ) instead. The importance of transition states involving ring-metal bond bending and ring tilting modes was manifest in the spectrum of the double bridged derivative (IV). Resonance absorption for the  $CH_2$  protons in IV appeared as a broad band centered at  $8.10 \tau$  with 2 smaller satellite bands suggesting an intermediate rate of chain inversion. The small spin splitting observed for ring proton resonance (major peak  $6.13 \tau$ ) was attributed to the rigid ring tilted conformation of IV which brings one proton on each of the rings considerably closer to the metal atom than the other two. The magnetic inequivalence of ring protons in I ( $R = R^1 = H$ ,  $R^2 = R^3 = Me$ ) (V) shown by triplets at  $\tau 5.93$ ,  $6.05$  ( $J \sim 2$  cycles/second is probably due to increase in the angle of ring tilt brought about by contraction of the internal valence angle by reason of the gem  $Me_2$  group. The rate of conformational exchange in III ( $R = R^1 = R^2 = R^3 = H$ ) (VI) must be considerably diminished since the  $\alpha$  and  $\beta$  bridge proton resonances appear as 2 structureless broad peaks at  $7.58$ ,  $8.17 \tau$ . The greater energy barrier derives from the requirement that chain inversion in VI, unlike that in II or V, necessitates passage of a  $CH_2$  group through the inside of the bridge.

77. Samitov, Y. Y. and Aminova, R. M.,  
NUCLEAR MAGNETIC RESONANCE SPECTRA OF FERRO-  
CENE COMPOUNDS AND MAGNETIC ANISOTROPY OF  
FERROCENE, Doklady Akademii Nauk SSSR, Vol. 156, No. 1,  
1964, pp. 142-144.

The proton chemical shifts of ferrocene, tributylferrocene, "bis-1, 1'-diferrocenyl-di-1, 1'-dicyclopentyl" (Nesmeyanov, et al., CA 60, 6367d), 1, 1'-diferrocenylethane, and 1, 2-diferrocenylethane, in a 20 volume percent solution in CS<sub>2</sub>, and of ethylferrocene (by extrapolation to infinite dilution), are tabulated. The spectrum of ethylferrocene shows a marked paramagnetic effect of the Et protons and the magnetic anisotropy of ferrocene is -49.5 cm.<sup>3</sup>/mole.

78. Schlogel, K. and Fried, M.,  
OPTICALLY ACTIVE HYDROCARBONS OF THE FERRO-  
CENE SERIES, Tetrahedron Letters, No. 22, 1963, pp. 1473-  
1478 (in German).

Refer to item No. 14 for abstract.

79. Schraml, J. and Voitlaender, J.,  
DESCRIPTION OF ELECTRIC FIELD GRADIENTS IN  
Fe (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> AND [Co (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>]<sup>+</sup> BY THE LIGAND FIELD  
THEORY, Zeitschrift für Naturforschung, Vol. 20a, No. 11,  
1965, pp. 1424-1430 (in German).

The electrical field gradients at the metal nuclei in the isoelectronic compounds Fe (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub> and [Co (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>]<sup>+</sup> are computed, using a modified electrostatic model (Ligand field theory). The direct contribution of the (<sup>1</sup>S3d<sup>6</sup>) state is diminished by the influence of the lattice, covalency, and Sternheimer polarization. The results are: at the CO<sup>3+</sup> site 1.81 and at the Fe<sup>2+</sup> 1.37 a. u., which are to be compared with the experimental ones, 1.67 and 1.25 (Q = 0.18b) or 0.78 (Q = 0.29b). The behavior of the 3d electrons in the strong crystalline field is also used to explain the spectra of ferrocene. The splitting of the 3d-orbital in the electrical field of the crystal is shown as a function of the distance metal-charge concentration of the π-electrons of the C<sub>5</sub>H<sub>5</sub> ring. The correlation energies are tabulated and the results given of the field gradient calculations.



80. Scott, D. R. and Becker, R. S.,  
LIGAND FIELD ABSORPTION BANDS AND D ORBITAL  
SPLITTING IN FERROCENE, Journal of Organometallic  
Chemistry, Vol. 4, No. 5, 1965, pp. 409-411.

The weak absorption bands in the ferrocene spectrum and the relative order of the d orbitals on the basis of a theoretical model have been assigned and determined. The ground state d configuration of ferrocene is assigned to be  $(a_{1g})^2 (e_{2g})^4 [{}^1A_{1g}]$ , in agreement with the majority of calculation and overlap considerations. The 1-electron excitations  $a_{1g} \rightarrow e_{1g}^*$  and  $e_{2g} \rightarrow e_{1g}^*$  produce excited states  ${}^1, {}^3E_{1g} (1)$  and  ${}^1, {}^3E_{1g} (2)$ ,  ${}^1, {}^3E_{2g}$ , respectively. The configuration interaction will mix the 2  ${}^1E_{1g}$  states and also the 2  ${}^3E_{1g}$  states. In the ligand field model, the excitation energies from the ground state to these excited states can be expressed in terms of the 1-electron orbital energies and the Slater-Condon parameters  $F_2$  and  $F_4$ . A successful overall fit to the experimental data is given with the following values for the parameter:  $Ds = 4960 \text{ cm.}^{-1}$ ,  $Dt = 3050 \text{ cm.}^{-1}$ ,  $F_2 = 923 \text{ cm.}^{-1}$ , and  $F_4 = 103 \text{ cm.}^{-1}$ . The standard deviation between the calculated and observed band maximum for all 6 bands is  $260 \text{ cm.}^{-1}$ . The assignment of the ligand field bands are:  ${}^1A_{1g} \rightarrow {}^1E_{1g}^+ (30.82 \text{ kK.})$ ,  ${}^1E_{2g}$  and  ${}^1E_{1g}^- (22.70 \text{ kK.})$ ,  ${}^1E_{1g}^+ (18.59 \text{ kK.})$ ,  ${}^1E_{2g} (16.10 \text{ kK.})$ , and  ${}^1E_{1g}^- (14.2 \text{ kK.})$  (kK. = kilokaysers). The experimental band with maximum at  $22.70 \text{ kK.}$  is composed of the 2 experimental unresolved overlapping transitions,  ${}^1E_{2g}$ ,  ${}^1E_{1g}^*$ . The agreement between the calculated and experimental data shows that these weak bands in the absorption spectrum of ferrocene are ligand field bands. The order of the d levels is  $e_{1g}^* > a_{1g} > e_{2g}$  with  $e_{1g}^* - a_{1g} = 25.5 \text{ kK.}$  and  $a_{1g} - e_{2g} = 4.59 \text{ kK.}$  The fitted values of  $F_2$  and  $F_4$  led to the nephelauxetic parameter,  $\beta = [F_2 - 5F_4 (\text{complex})] / [F_2 - 5F_4 (\text{free ion})]$ , for ferrocene. By using B (free ion) for  $\text{Fe}^{2+} = 1058 \text{ cm.}^{-1}$ ,  $\beta = 0.39$ . This value places the  $\text{C}_5\text{H}_5$  ligand near or above  $\text{CN}^-$  in the nephelauxetic series.

81. Shustorovich, E. M. and Dyatkina, M. E.,  
THE ELECTRONIC STRUCTURE OF FERROCENE, Zhurnal  
Stukturnoi Khimii, Vol. 7, No. 1, 1966, pp. 139-140 (in  
Russian), Chemistry of the Iron Group Metallocenes: Ferrocene,  
Ruthenocene, Osmocene, New York, New York, J. Wiley and Sons,  
pt. 1, 1965, p. 23.

Refer to item No. 29 for abstract.

82. Smith, F. J.,

STUDIES IN MOLECULAR SPECTROSCOPY, I. EXCIMER FLUORESCENCE, II. HEAVY-ATOM SPIN-ORBITAL COUPLING EFFECT, AND III. THE ELECTRONIC SPECTRA OF FERROCENE, University Microfilms (Ann Arbor, Michigan) Order No. 66-748, 115 pp., Dissertation Abstracts, Vol. 26, No. 8, 1966, p. 4274.

The interpretation of the energies of excimer luminescence of naphthalene and twelve of its alkyl derivatives is considered, and it is shown that there is considerable configuration interaction between molecular exciton and charge resonance states and that the energy of excimer fluorescence may not be interpreted without invoking this configuration interaction. The energies of excimer fluorescence are calculated for the substituted naphthalenes using a four-electron MO treatment of the interaction as a function of  $Z$ , the effective nuclear charge to be used in a Slater orbital exponent, and of the interplanar distance  $D$ . Agreement with excimer luminescence energies is obtained for values of  $Z = 3.18$  and values of  $D$  between 3.45 and 3.7 Å, with the largest intermolecular distance  $D$  being obtained for those compounds in which the steric hindrance is expected to be largest.

The delayed fluorescence and delayed excimer fluorescence of pyrene in liquid solution are shown to originate in triplet-triplet annihilation, and the triplet population is shown to be kinetically limited by first order decay mechanisms. It is shown that the delayed excimer fluorescence of pyrene crystal at 77°K also originates in triplet-triplet annihilation, but that the triplet population is kinetically governed by second order annihilative processes. It is also shown that at lower temperatures and higher viscosities triplet-triplet annihilation results predominantly in the initial production of excited monomers, whereas at higher temperatures the initial production of excimers also becomes an important process.

The relative phosphorescence to fluorescence quantum yields and phosphorescence lifetimes of naphthalene have been measured in a number of glassy media, some of which contain perturbing atoms of large atomic number. It is shown that the intersystem crossing process is the most sensitive to environmental spin-orbital coupling effects. The phosphorescence quenching process is less sensitive than the intersystem crossing process, but more sensitive than the phosphorescence emission process. It is strongly suggested by the data contained herein that heavy atom quenching of fluorescence can indeed be attributed primarily, if not entirely,

to increase in the probability of the intersystem crossing process. A number of possible uses for the heavy atom technique are suggested.

A total of eight singlet-singlet transitions are observed in the Ferrocene Vapor spectra. Transitions at 42,181, 46,933 and 53,078  $\text{cm}^{-1}$  are reported for the first time. Vibrational analyses of the vapor spectrum are given and assignments of the electronic transitions are made.

83. Starovskii, O. V. and Struchkov, Y. T.,  
THE STRUCTURE OF FERROCENEDISULFONYL CHLORIDE,  
Zhurnal Strukturnoi Khimii, Vol. 5, No. 2, 1963, pp. 257-  
260 (cf. CA 56, 11029a).

A more accurate determination is made of the structure of  $\text{Fe}(\text{C}_5\text{H}_4\text{SO}_2\text{Cl})_2$  by using the method of least squares and 3-dimensional data. The at. coordinates were obtained from the 3-dimensional series of electron d. The interat. distances and valence angles are tabulated.

84. Texas University, Department of Physics, Austin, Texas,  
MÖSSBAUER STUDIES OF IRON ORGANOMETALLIC COM-  
PLEXES. IV. SIGN OF THE ELECTRIC FIELD GRADIENT  
IN FERROCENE by R. L. Collins, 1964, AD-617 523  
(Unclassified Report).

The quadrupole splitting of  $\text{Fe}^{57}$  Mossbauer spectra gives the magnitude, but not the sign, of the electric field gradient. The sign can be determined by magnetically perturbing the energy levels, so that one line splits into a triplet and the other line splits into a doublet. A first-order perturbation treatment for the axially symmetric electric field gradient case is given for powdered samples.

The method is applied to ferrocene, which has been the subject of many theoretical papers. A crystal field treatment predicts a positive electric field gradient, and molecular orbital treatments predict negative electric field gradient's. At 40 kilogauss applied, the two lines split clearly into a doublet and a triplet. The result agrees with the molecular orbital treatment. This also explains the essential vanishing of the electric field gradient in ferrocinium compounds.

85. Benkeser, R. A.,  
CHEMISTRY OF FERROCENE AND RELATED COMPOUNDS,  
Scientific Technical Aerospace Report, Vol. 2, No. 24,  
1964, p. 3500, CFSTI, 1963, 16 pp. (AD 600 969, N64-32822).

A series of ferrocene compounds containing a carboxyl group in one of the rings and a variety of other electron supplying and withdrawing groups in the other ring were synthesized. Free radical addition reactions to the vinyl-ferrocene group in view of obtaining new types of ferrocene compounds were studied and demonstrated by equations. Methods of decomposing substituted ferrocenes into their parent cyclopentadienes with the principal purpose of working out a method for identifying new ferrocene structures were discussed. A study was made of the metalation of various alkylferrocenes with amylsodium. A competitive metalation between ferrocene and benzene was carried out with a limited amount of amylsodium.

86. Gubin, S. P., Shepilov, I. P., and Nesmeyanov, A. N.,  
ACETYLATION OF FERROCENE WITH  $2\text{AcOH} \cdot \text{BF}_3$  COMPLEX,  
Izvestia Akademii Nauk SSSR, Seriya Khimicheskaya, No. 2,  
1966, p. 384 (in Russian).

Acetylation of ferrocene by  $2\text{AcOH} \cdot \text{BF}_3$  in AcOH was studied kinetically. The following rate constructions were determined as  $k_1 \times 10^6 \text{ sec.}^{-1}$ : at  $40^\circ$  0.8; at  $45^\circ$  1.9; at  $50^\circ$  3.8; at  $55^\circ$  7.5, for pseudo-first order reaction. The apparent activation energy was 22.4 kcal./mole. Ferrocene was 200-300 times more active than MeOPh in acetylation reaction.

87. Hooz, J.,

FACTORS GOVERNING ORIENTATION IN METALATION REACTIONS: PART I. METALATION OF ETHYLBENZENE, PART II. METALATION OF CUMENE, PART III. STRUCTURE ELUCIDATION OF ACETYLBUTYLFERROCENES BY NMR SPECTROSCOPY, PART IV. ISOMER DISTRIBUTIONS, RELATIVE SITE REACTIVITIES AND PARTIAL RATE FACTORS FOR THE ACETYLATION OF METHYL-, ETHYL-, ISOPROPYL- AND t-BUTYLFERROCENE, University Microfilms (Ann Arbor, Michigan), Order No. 64-4003, 222 pp., Dissertation Abstracts, Vol. 24, No. 12, 1964, p. 4998.

#### PART I

Ethylbenzene is metalated predominantly by n-amylsodium and n-amylpotassium initially in the aromatic ring. The ring carbanions thus formed transmetalate ethylbenzene to give a predominance of  $\alpha$ -product at longer reaction times. Orientation is not necessarily governed by the mode of preparation of alkylalkali reagent. These findings are in accord with a mechanism involving nucleophilic attack on hydrogen.

#### PART II

The isomer distributions observed by metalating cumene with n-amylpotassium are not a function of the manner in which the organometallic is prepared. Initial attack occurs on ring hydrogens. The m- and p-phenylisopropylpotassium compounds thus produced act as metalating agents toward excess cumene.  $\alpha$ -cumylpotassium predominates at long reaction times. Under similar conditions,  $\alpha$ -cumylsodium is unstable;  $\alpha$ -methylstyrene is formed as one of the decomposition products. The  $\alpha$ -methylstyrene generated undergoes further metalation and dimerization.

#### PART III

The isomeric methyl-, ethyl-, isopropyl- and t-butylacetylferrocenes have been prepared and their nuclear magnetic resonance spectra recorded. It was found that the absorptions observed should serve as a useful fingerprint for structure determinations of homoannularly disubstituted

acetylalkylferrocenes. The ultraviolet and infrared absorption spectra were recorded and compared with existing correlations.

#### PART IV

Isomer distributions for the acetylation of the homologous alkylferrocenes have been determined. The relative rates of reaction,  $k(\text{alkylferrocene})/k(\text{ferrocene})$ , were determined competitively, using vapor phase chromatography to analyze the reaction products. Partial rate factors for the acylation reaction have been determined. A comparison with the corresponding alkylbenzenes has been made.

88. Komenda, J.,  
STRUCTURAL EFFECTS IN THE OSCILLOGRAPHIC  
POLAROGRAPHY OF FERROCENES, Chemicke Zvesti,  
Vol. 18, 1964, pp. 378-384 (in German).

Ferrocene and its derivatives in  $M \text{ HClO}_4$  in 50 percent EtOH, using a rotating Pt electrode, produced anodic pulses.  $Q$  values were tabulated and compared with Hammett's  $\sigma_p$  constructions of individual substituents. They showed a linear relation, except for some deviation by mesomerism. The oscillographic behavior of chalcones substituted with ferrocene was explained.

89. Little, W. F., Berry, R. A., and Kannan, P.,  
BASICITIES OF FERROCENYL AZOBENZENES, American Chemical Society Journal, Vol. 84, 1962, pp. 2525-2529.

The  $pK_a$  values for the conjugate acids of a series of substituted *m*- and *p*-ferrocenylazobenzenes were measured in aqueous sulfuric acid containing 20 volume-percent ethanol. In each case, the ferrocenylazobenzene was a weaker base than the corresponding parent azobenzene; i. e., the ferrocenyl group in this study behaves as an electron-withdrawing group, in contrast to its behavior as an electron-donating group in other studies. Evidence is presented for prior protonation of the ferrocene nucleus to account for the weaker basicity of the azo linkage in these systems. Hammett  $\sigma$ -constructions were obtained for the protonated ferrocenyl group in the *m*- and *p*-positions, and Hammett  $\rho$ - $\sigma$  correlations discussed in the light of earlier work of Jaffe with azobenzenes.

90. Marr, G. and Webster, D. E.,  
ELECTROPHILIC REACTIVITY OF (TRIMETHYLSILYL)  
FERROCENE, -RUTHENOCENE, AND -OSMOCENE, Journal  
of Organometallic Chemistry, Vol. 2, No. 1, 1964, p. 99.

The first-order rate constructions ( $10^3 k_1 \text{ min.}^{-1}$ ) for the cleavage of the cyclopentadiene-Si bond in  $\text{Me}_3\text{SiC}_5\text{H}_4\text{-MC}_5\text{H}_5$  (M = metal) in MeOH and aqueous HCl (0.596 and 0.477 M, respectively) were: Fe, 3.36, 2.45; Ru, 156.5, 109.3; and Os, 62.66, 48.10.

91. Mulay, L. N. and Attalla, A.,  
ACTIVATION ENERGIES FOR REORIENTATION PROCESSES  
IN FERROCENE AND SOME OF ITS DERIVATIVES. A STUDY  
OF PROTON MAGNETIC RESONANCE SPECTRA, American  
Chemical Society Journal, Vol. 85, 1963, pp. 702-706,  
Naturwissenschaften, Vol. 50, 1963, p. 151.

The proton magnetic resonance spectra of ferrocene and some of its typical derivatives were studied over a wide temperature range (78-300°K.) by using a Pound-Knight-Watkins-type oscillator and a special cryostat. The line width ( $\delta H$ ) and the second moment ( $(\Delta H)^2$ ) data were interpreted to elucidate the reorientation processes of the cyclopentadienyl rings and the influence of the substituents on such processes. Some derivatives with completely deuterated substituents were specially studied to eliminate any contribution to the absorption curves obtained for the protons. In general,  $\delta H$  and  $(\Delta H)^2$  increased with increased substitution at corresponding temperatures; the broadening arising from interactions between the protons of the cyclopentadienyl rings and the nuclei of the substituents is also discussed. The plots of  $\delta H$  versus temperature were used to evaluate the correlation time  $\tau_0$  at certain temperatures. The magnitudes of the activation energy  $E_a$  for the reorientation processes were calculated therefrom. These range from 2.3 kcal./mole for ferrocene to 5.0 kcal./mole for diperdeuterioacetylferrocene and are seen to increase with increasing substitution in one or both rings.

92. Nesmeyanov, A. N. and Reutov, O. A.,  
EFFECT OF SUBSTITUENTS ON THE ACID STRENGTH OF  
FERROCENECARBOXYLIC ACIDS, Doklady Akademii  
Nauk SSSR, Vol. 115, 1957, pp. 518-521.

Adding 5 g. Me ferrocenecarboxylate (I) to 5 g.  $AlCl_3$ , 2.35 g.  $AcCl$ , and 30 ml.  $CCl_4$  at  $10^\circ$ , stirring 1 hr. and treating with ice gave 58 percent Me acetylferrocenecarboxylate, m.  $92.5-4.5^\circ$  hydrolyzed with 20 percent NaOH to the free acid (II), m.  $153-5^\circ$  ( $C_6H_6$ ),  $pK_a$  5.91 (68 percent MeOH at  $20^\circ$ ), which with Zn-Hg in AcOH gave 70 percent ethylferrocenecarboxylic acid, m.  $75.5-7.5^\circ$ ,  $pK_a$  6.43. Me butyrylferrocenecarboxylate, prepared as above, in 45 percent yield, m.  $54.5-5.5^\circ$ , was hydrolyzed to the free acid, m.  $114-15^\circ$  ( $CCl_4$ -MeOH),  $pK_a$  5.95, reduced as above to butylferrocenecarboxylic acid, m.  $73-4.5^\circ$ ,  $pK_a$  6.50. Heating 0.7 g. II and 0.9 g. iodine in 1 ml. pyridine 2 hrs. at  $100^\circ$ , dilg. with  $H_2O$ , heating, filtering, precipitating the crude acids with HCl, and bleaching the starting material with  $C_6H_6$  gave 0.1 g. crude ferrocenedicarboxylic acid, yielding with  $CH_2N_2$  0.06 g. di-Me ester, m.  $114-15^\circ$ ; this heated 50 min. with aqueous NaOH-MeOH gave 24.5 percent mono-Me ester, m.  $147.5-9.50$ ,  $pK_a$  6.08. Sulfonation of I with dioxane- $SO_3$  in  $(CH_2Cl)_2$  at  $0^\circ$  24 hrs. and treatment with  $CH_2N_2$  in  $Et_2O$  gave 34 percent di-Me ferrocenesulfo-carboxylate, m.  $93-5^\circ$  (ligroine-MeOH). An equimolar mixture of ferrocene and ferrocenecarboxylic acid with dioxane- $SO_3$  in  $(CH_2Cl)_2$  at  $5^\circ$  (finally at  $20^\circ$ ) gave 10 percent unreacted ferrocene and 94 percent unreacted ferrocene-carboxylic acid,  $pK$  6.29; benzylthiuronium salt, m.  $219-21^\circ$ . The  $pK$  values shown above were obtained from potentiometric data at three stages of neutralization.

93. Nesmeyanov, A. N. and Perevalova, E. G.,  
"NEW AROMATIC SYSTEMS" 1-FERROCENE AS AN ARO-  
MATIC SYSTEM, Khim. Nauka i Prom., Vol. 3, 1958,  
pp. 146-158.

A general discussion of the aromatic nature of the cyclopentadiene ring of ferrocene.



94. Nesmeyanov, A. N., Kursanov, D. N., Setkina, V. N., Kislyakova, N. V., and Kochetkova, N. S.,  
HYDROGEN EXCHANGE REACTIONS OF NON-BENZENOID AROMATIC SYSTEMS (CENES). I. HYDROGEN EXCHANGE OF FERROCENE AND MONO AND DIACETYLFERROCENE WITH ACIDS, Izvestia Akademii Nauk SSSR, Seriya Khimicheskaya, 1962, pp. 1932-1936 (cf. CA 55, 14418e; CA 57, 5938d).

Ferrocenes exchange H with  $\text{CCl}_3\text{CO}_2\text{D}$  in glacial AcOD,  $\text{D}_2\text{SO}_4$ , DCl, or  $\text{CF}_3\text{CO}_2\text{D}$ . Oxidation to the non-exchanging ferricinium ion occurs in  $\text{D}_2\text{SO}_4$ . The first order rate constructions in  $\text{sec.}^{-1}$  for H exchange with  $\text{CF}_3\text{CO}_2\text{D}$  in  $\text{C}_6\text{H}_6$  solution at  $25^\circ$  are: ferrocene,  $1.6 \times 10^{-4}$ ; acetylferrocene,  $1.5 \times 10^{-7}$ ; 1, 1'-diacetylferrocene,  $7.7 \times 10^{-8}$ ; and PhMe,  $3 \times 10^{-8}$ .

95. Nesmeyanov, A. N., Romanenko, V. I., and Sazonova, V. A.,  
BASICITY CONSTANTS OF FERROCENE AMINES, Izvestia Akademii Nauk SSSR, Seriya Khimicheskaya, No. 2, 1966, pp. 357-358 (in Russian).

The following  $K_b$  values were calculated from the potentiometric titrn. of ferrocene amines in 80 percent aqueous EtOH: ferrocenamine  $4.05 \times 10^{-11}$ ; ethylferrocenylamine  $7.07 \times 10^{-11}$ ; diethylferrocenylamine  $1.22 \times 10^{-11}$ ; 1, 1'-chloroferrocenylamine  $7.46 \times 10^{-12}$ ;  $\alpha$ -pyridylferrocene  $1.02 \times 10^{-12}$ .

96. Pavlik, I. and Handlíř, K.,  
DONOR-ACCEPTOR COMPLEXES OF 1, 1'-DIACETYL-FERROCENE WITH ALUMINUM CHLORIDE, ALUMINUM BROMIDE, AND TITANIUM CHLORIDE, Collection of Czechoslovak Chemical Communications, Vol. 31, No. 5, 1966, p. 1958.

Not abstracted.

97. Rosenblum, M. and Howells, W. G.,  
STRUCTURE AND CHEMISTRY OF FERROCENE. V. INTRAANULAR ELECTRONIC EFFECTS, American Chemical Society Journal, Vol. 84, 1962, pp. 1167-1172 (cf. CA 54, 4528d).

A series of 1, 1'-diarylferrocenes was acetylated under Friedel-Crafts conditions, and relative site reactivities were

determined. The 2-position in the arylferrocenes studied was more reactive than the 3-position, but in general aryl substituents inductively deactivated the ferrocene ring to which they were bonded. The compound or mixture was dissolved in 15 ml. dry  $\text{CH}_2\text{Cl}_2$  and 15 ml.  $\text{AcCl}$  (I). The solution was cooled and stirred while a molar equivalent of  $\text{AlCl}_3$  in I was added dropwise during 15 min. After 1 hr. at  $0^\circ$  the mixture was poured into a solution of  $\text{NaHSO}_3$  in 100 ml. saturated  $\text{NaCl}$ . After extraction the aqueous phase was repeatedly extracted with  $\text{Et}_2\text{O}$  until the  $\text{Et}_2\text{O}$  extract was colorless. The organic phases were combined and washed with  $\text{NaOH-NaCl}$  and then  $\text{NaCl}$  solutions until neutral. The solution was dried over  $\text{MgSO}_4$ , filtered, washed with  $\text{Et}_2\text{O}$  until colorless, and concentrated to about 10 ml. The fractions were separated on an alumina column, using  $\text{Et}_2\text{O}$  for elution. The following acetylferrocenes were thus prepared (melting point and recrystallization solvent given): 2-acetyl-1, 1'-bis (p-methoxyphenyl) ferrocene, - (oil), -; 3-acetyl-1, 1'-bis (p-methoxyphenyl) ferrocene,  $147-8^\circ$ , cyclohexane; 2-acetyl-1, 1'-bis (p-bromophenyl) ferrocene,  $126.5-7.5^\circ$ , Skellysolve B (II); 3-acetyl-1, 1'-bis (p-bromophenyl) ferrocene,  $145-7^\circ$ , II; 1-acetyl-1'- (p-methoxyphenyl) ferrocene,  $97-8^\circ$ , petr. ether (b.  $38-52^\circ$ ); 2-acetyl-1- (p-methoxyphenyl) ferrocene,  $137-9^\circ$ , II. 3-ethyl-1, 1'-diphenylferrocene, m.  $88-90^\circ$ , was prepared by Clemmensen reduction of 3-acetyl-1, 1'-diphenylferrocene in glacial  $\text{AcOH}$  with  $\text{Zn}$  dust and  $\text{HCl}$ .

98. Rosenblum, M. and Abbate, F. W.,  
 PARTICIPATION OF THE METAL ATOM IN THE REACTIONS  
 OF THE IRON GROUP METALLOCENES, Abstracts, 152  
 ACS Meeting, Section 0, No. 138, New York, September 1966.

Refer to item No. 13 for abstract.

## A. Ferrocene, Bridged Ferrocenes, and Multinuclear Ferrocenes

99. Applebaum, M. N., Fish, R. W., and Rosenblum, M.,  
DEHYDRO-1, 1'-TRIMETHYLENEFERROCENE, Journal of  
Organic Chemistry, Vol. 29, No. 8, 1964, pp. 2452-2453.

The transformation of  $\alpha$ -oxo-1, 1'-trimethyleneferrocene to silyldrazone (I) under conditions of the Bamford-Stevens reaction was examined. Irradiation of I under normal conditions failed to give any well-defined products. Thermal decomposition in  $\text{Me}_2\text{SO}$  with NaOMe gave the ketone (II) and 1, 1'-trimethyleneferrocene (III). But thermal



decomposition in cyclohexane in the presence of either NaOMe or NaH gave moderate yields of dehydro-1, 1'-trimethyleneferrocene (IV). Conversion of IV into III was achieved by catalytic hydrogenation. I with ethoxyethane gave II and  $\alpha$ -methoxy-1, 1'-trimethyleneferrocene. The ultraviolet spectrum of IV compared with that of III showed the absence of conjugation between the ethylenic bond and the cyclopentadienyl ring in IV.

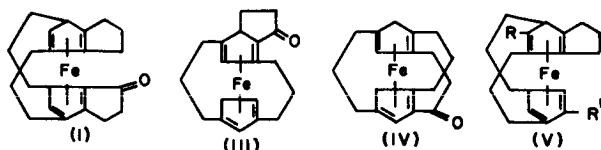
100. Brantley, J. C.,  
ORGANO-TRANSITION ELEMENT COMPOUNDS, U. S.  
Patent 3,028,406, 3 April 1962, Applied 25 July 1955, 3 pp.

The preparation of compounds having the general formula  $\text{R}_2\text{MX}$ , is described where R is cyclopentadienyl or a cyclopentadienyl-containing moiety, M is a transition element such as Sc, Ti, V, Cr, Mn, Fe, Ni, or Co, X is halogen, and z may vary from 0 to 3. Interaction of an alkaline-earth metal carbide with R yields the metal cyclopentadienyl necessary for reaction with the transition element halide. Thus, to 16 g.  $\text{CaC}_2$  finely pulverized under N and 225 ml. liquid  $\text{NH}_3$  was added dropwise 47.1 ml. cyclopentadiene. After stirring 1 hr., 200 ml.  $(\text{CH}_2\text{OMn})$  was added and  $\text{NH}_3$

removed by warming to room temperature. After cooling the mixture in an ice bath, 27 g. anhydrous  $\text{FeCl}_3$  was added. After careful hydrolysis of the mixture with  $\text{EtOH}$  then diluted aqueous  $\text{HCl}$  the product was extracted with  $\text{C}_4\text{H}_4$ . Evaporation of the solvent followed by recrystallization from petr. ether gave bis (cyclopentadienyl) iron in 11.8 percent yield based on the  $\text{CaC}_2$  used.

101. Bublitz, D. E. and Rinehart, K. L., Jr.,  
1, 1': 3, 3': 4, 5: 4', 5'-TETRAKIS (TRIMETHYLENE)  
FERROCENE, Tetrahedron Letters, No. 15-16, 1964,  
pp. 827-833 (cf. CA 59, 658h).

4'-Acetyl-1, 1': 3, 3': 4, 5-tris (trimethylene) ferrocene was treated with  $\text{NaH}$  and  $\text{CO}(\text{OEt})_2$ , and the resulting  $\beta$ -oxo ester hydrogenolyzed in  $\text{HOAc}$  in the presence of  $\text{PtO}_2$  to the Et 4'-propionate, which on hydrolysis with  $\text{NaOH}$  gave the 4'-propionic acid. The last on ring closure in  $\text{CCl}_4$  in the presence of  $(\text{CF}_3\text{CO})_2\text{O}$  gave the cyclized ketone 4', 5'-( $\alpha$ -oxotrimethylene)-1, 1': 3, 3': 4, 5-tris (trimethylene) ferrocene (I), m. 195-5.8°. Its structure was confirmed by its infrared and nuclear magnetic resonance spectra. Reduction of I with  $\text{LiAlH}_4\text{-AlCl}_3$  gave 1, 1': 3, 3': 4, 5: 4', 5'-tetrakis (trimethylene) ferrocene, m. 156.5-59°, whose symmetrical nature was shown by its spectrum.



Schlogel and Peterlik (CA 57, 15151a; 59, 3952g) cyclized 2, 2': 5, 5'-bis (trimethylene) ferrocene-4-propionic acid (II) to give two cyclic ketones. A, m. 159-60°, and B, m. 185-8°, shown to have structures III and IV, respectively, and not those assigned by Schloegl and Peterlik (A number of typographical errors in the two publications of Schloegl and Peterlik were pointed out.) Formylation of 1, 1': 3, 3': 4, 5-tris (trimethylene) ferrocene gave a mixture of V ( $\text{R} = \text{CHO}$ ,  $\text{R}' = \text{H}$ ), m. 124.5-27°, and V ( $\text{R} = \text{H}$ ,  $\text{R}' = \text{CHO}$ ), m. 107-9.5°, in the ratio of 3 to 1. The structures of the 2 isomers were proved by their nuclear magnetic resonance spectra.

102. Bulloff, J. J.,

ALKALI METAL AND ALKALINE EARTH METAL CYCLO-PENTADIENYLS AND TRANSITION METAL COMPOUNDS DERIVED THEREFROM, U. S. Patent 3, 030, 393, 17 April 1962, Applied 21 March 1955, 2 pp.

An alkali or alkaline earth metal hydride reacts with cyclopentadiene (I) to form H and the cyclopentadienide, which reacts further to give cyclopentadienyl-transition metal derivatives. For example, 66 g. I was dissolved in 1 l. "Amsco Naphthol Mineral Spirits" and 24 g. NaH added. When H evolution had ceased, 160 g.  $\text{FeCl}_3$  was added slowly. The solution was filtered, the solvent removed in vacuo, and  $(\text{C}_5\text{H}_5)_2\text{Fe}$  sublimed from the vessel at 1.5 mm., yield 160 g. A second reaction, using tetrahydrofuran as solvent and 127 g.  $\text{FeCl}_2$ , and isolation of the product by crystallization, gave 132 g.  $(\text{C}_5\text{H}_5)_2\text{Fe}$ . Finally, 80 g.  $(\text{C}_5\text{H}_5)_2\text{Ca}$ , prepared as was the Na compound above and isolated by removal of solvent, was spread on a fine mesh screen, which was inserted into a pipe together with 360 g.  $\text{TaCl}_5$ . The pipe was capped, evacuated, and heated for 6 hrs. The tube was opened and the crude product shaken from the screen. Recrystallizing from  $\text{CHCl}_3$  gave 2 oz.  $(\text{C}_5\text{H}_5)_2\text{TaCl}_3$ .

103. Decombe, J., Dormond, A., and Ravoux, J. P.,

SEVERAL NEW DERIVATIVES OF FERROCENE, Comptes Rendus, Vol. 259, No. 23, 1964, pp. 4289-4291 (in French).

Fe = ferrocenyl. The reaction of  $\text{FeCH}_2\text{NMe}_2\text{I}$  (I) with  $\text{Ac}_2\text{CH}_2$  in  $\text{Me}_2\text{NCHO}$  (DMF) gave 70 percent  $\text{FeCH}_2\text{CHAc}_2$  (II), m.  $52^\circ$ . A small quantity of  $\text{Ac}_2\text{C}(\text{CH}_2\text{Fe})_2$  (III), m.  $178^\circ$ , was formed as a by-product. Attempted purification of II by chromatography on  $\text{Al}_2\text{O}_3$  led to partial decomposition with the formation of  $\text{FeCH}_2\text{CH}_2\text{Ac}$  (IV), m.  $43^\circ$ . A similar reaction of I with  $\text{PhCH}_2\text{CN}$  gave 35 percent  $\text{FeCH}_2\text{CHPhCN}$



(V), m.  $105^\circ$ . Heating V with alcoholic KOH followed by acidification gave 85 percent  $\text{FeCH}_2\text{CHPhCO}_2\text{H}$  (VI), m.  $98-9^\circ$ . Heating VI with  $(\text{CF}_3\text{CO})_2\text{O}$  in  $\text{CH}_2\text{Cl}_2$  gave VII, m.  $183^\circ$ .  $\text{Ph}_2\text{CHCN}$  reacted with I in DMF to give 76 percent  $\text{FeCH}_2\text{CPh}_2\text{CN}$  (VIII), m.  $137^\circ$ . Attempts to convert VIII into the corresponding acid were unsuccessful. The reaction of  $\text{EtO}_2\text{CCH}_2\text{COCO}_2\text{Et}$  with I gave a complex mixture containing

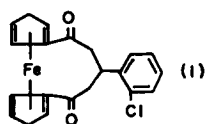
at least four substances. However, the only species isolated in identifiable amounts was  $(\text{FeCH}_2)_2\text{C}(\text{CO}_2\text{Et})\text{COCO}_2\text{Et}$  (IX), m.  $95^\circ$ , in 27 percent yield. Treatment of IX with alcoholic KOH followed by acidification gave  $(\text{FeCH}_2)_2\text{CHCOCO}_2\text{H}$  (X), m.  $167^\circ$ . Treatment of X with  $(\text{CF}_3\text{CO})_2\text{O}$  in  $\text{CH}_2\text{Cl}_2$  gave XI, m.  $220^\circ$ .

104. Freeman, D. C., Jr. and Thomas, T. L., Jr.,  
ORGANOMETALLIC COMPOUNDS, U. S. Patent 3,032,569,  
1 May 1962, Applied 9 April 1956, 4 pp.

Dicyclopentadienyliron (I) and related substances are produced in a vapor-phase reaction between the metal halide and the cyclopentadienyl compound in an inert carrier gas stream.  $\text{FeCl}_2$  and cyclopentadiene (II) yield in a single pass 68 percent of I, based on applied iron, or 5.2 percent I, based on applied II at a reaction temperature of  $400\text{-}500^\circ$ . Analogous compounds of Ni and Co were made.

105. Furdik, M. and Toma, S.,  
DERIVATIVES OF FERROCENE VI. ACID-CATALYZED  
ALDOL CONDENSATION AND INTRAMOLECULAR MICHAEL  
CONDENSATION OF 1,1-DIACETYLFERROCENE AND  
o-CHLOROBENZALDEHYDE, Acta Fac. Rerum Nat.  
Univ. Comenianae, Chimia, Vol. 7, 1963, pp. 545-547  
(In Slovak) (cf. CA 59, 1011a).

1,1'-Diacetylferrocene (1.5 g.) and 1.5 g. o-chloro-benzaldehyde were dissolved in 50 cc. MeOH, the solution

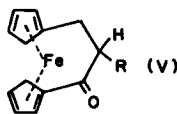


was heated to  $55^\circ$ , and 5 cc. concentrated HCl added slowly. The mixture was stirred for 9 hrs. at  $55^\circ$ , MeOH distilled in vacuo, and the residue crystallized from dioxane to give 0.5 g. 1,1'-[ $\alpha$ ,  $\alpha'$ -dioxo- $\gamma$ -(o-chlorophenyl)pentamethylene] ferrocene (I), m.  $267\text{-}9^\circ$ . The probable reaction mechanism was described.

106. Gautheron, B. and Tirouflet, J.,  
HETEROBRIDGED KETONES DERIVED FROM FERROCENE,  
Comptes Rendus, Vol. 258, No. 26, 1964, pp. 6443-6445.

In this abstract Z = ferrocenyl radical ( $\text{C}_5\text{H}_5\text{FeC}_5\text{H}_4^\cdot$ ).  
The sodio derivative of a substituted Et malonate,

$\text{RCH}(\text{CO}_2\text{Et})_2$  was prepared in xylene, powder  $[\text{ZCH}_2\text{NMe}_3]^+ \text{I}^-$  was added, and the product,  $\text{ZCH}_2\text{CR}(\text{CO}_2\text{Et})_2$ , was isolated by chromatography on  $\text{Al}_2\text{O}_3$  [ $\text{R} = \text{Me}$  (I), m.  $62^\circ$ ;  $\text{R} = \text{Ph}$  (II), m.  $81^\circ$ ]. I was saponified to form  $\text{ZCH}_2\text{CHMe}(\text{CO}_2\text{H})_2$  decomposed  $198^\circ$ , which was decarboxylated to give  $\text{ZCH}_2\text{CHMeCO}_2\text{H}$  (III), m.  $112^\circ$ ; II similarly gave directly  $\text{ZCH}_2\text{CHPhCO}_2\text{H}$  (IV), m.  $98^\circ$ . III or IV with  $(\text{CF}_3\text{CO})_2\text{O}$  gave V ( $\text{R} = \text{Me}$  m.  $102^\circ$ ;  $\text{R} = \text{Ph}$  m.  $186^\circ$ ). The structures of the heterobridged ketones were established by mass, infrared, and



ultraviolet spectroscopy. The influence of the gem dialkyl group in promoting the latter reaction is attributed to steric effects. Polarographic measurements on the ketones did not show the expected inhibition of resonance of CO.

107. Goldberg, S. I., Mayo, D. W., and Alford, J. A.,  
MULTI-NUCLEAR FERROCENES. I. BIFERROCENYL,  
Journal of Organic Chemistry, Vol. 28, 1963, pp. 1708-1710.

Additional evidence in confirmation of the structure of biferrocenyl (I) was presented. Isolation of I from the complex reaction mixtures was illustrated. After preparation of a mixture of lithio- and dilithioferrocene by reaction of 18 g. ferrocene (II) with  $\text{BuLi}$ , then treatment with 35 g. trihexylbromosilane, the reaction mixture was distilled to give a forerun,  $b_{0.2}$   $150-65^\circ$ , and trihexylsilylferrocene (III),  $b_{0.05}$   $184-7^\circ$ . At pot temperatures of  $200-20^\circ/0.05$  mm., I appeared as a sublimate, crystallized from  $\text{CHCl}_3$  to give 0.11 percent I, m.  $227.5-9.0^\circ$ . III (5.00 g.) slowly heated to  $220^\circ$  darkened and decomposed rapidly near  $250^\circ$ . The sublimate formed afforded 16 percent II but no I. Similar treatment of another sample of III, except that heating was carried out under N, caused the material to reflux with no signs of decomposition. Iodoferrocene (20 g.) and 40 g. Cu bronze placed in a flask, flushed with N for 0.5 hr. at room temperature, then heated to  $90^\circ$  under N, cooled, extracted

with warm  $C_6H_6$ , and the  $C_6H_6$  evaporated gave by fractional crystallization 7.5 g. I and 2.9 g. II. Infrared measurements at the 9 and 10  $\mu$  bands were carried out on the following compounds, which were of anal. purity: II, I, m-tolylferrocene, diferrocenyl ketone, 2-biphenylferrocene,  $\alpha$ -hydroxyethylferrocene, diferrocenylmercury, palmitoylferrocene, hexadecylferrocene, chloromercuriferrocene, trimethylsilylferrocene, benzoylferrocene, benzylferrocene, p-phenoxyphenylferrocene, and acetylferrocene.

108. Hata, K., Motoyama, I., and Watanabe, H.,  
THE DIRECT FORMATION OF BIFERROCENYL AND  
POLYFERROCENYLS FROM FERROCENYLLITHIUM,  
Chemical Society Bulletin, Japan, Vol. 37, 1964, p. 1719.

Although many synthetic methods of biferrocenyl have been proposed, all of these routes are circuitous and troublesome. Moreover, the formation of polyferrocenyls other than biferrocenyl has never been reported. The present authors wish to report on the direct formation of biferrocenyl and polyferrocenyls from ferrocenyllithium.

109. Holzappel, H., Huebner, H., Geissler, C., and Rolle, W.,  
FERROCENE, German (East) Patent 43,979 (Cl. C 07f),  
15 December 1965, Applied 7 January 1965, 2 pp.

$Fe(CO_2)_2 \cdot 2H_2O$  (30 g.) in a  $30 \times 2$ -cm. tube heated slowly under a N stream to  $200^\circ$ , and kept about 40 min. at  $200^\circ$ , cyclopentadiene added at 1 drop/2-4 sec. while simultaneously heating to  $380^\circ$ , the N stream replaced by CO, and the temperature increased after about 2 hrs. by  $20^\circ$  yielded about 20 g. ferrocene.

110. Iowa State University, Iowa City, Iowa,  
THE STRUCTURE OF OLEFIN-METAL COMPLEXES by  
N. C. Baenziger and J. R. Doyle, February 1961, Report  
No. AROD-1952-5, AD-254 703, Contract No. DA11 022ORD2647  
(Unclassified Report).

Contents: Preparative studies; complexes containing bicycloheptadiene; (norbornadiene); olefin-silver complexes; olefin-copper complexes; olefin-platinum complexes; olefin-mercury compounds; olefin-nickel complexes diffraction studies; bicycloheptadiene-bis-silver nitrate; tetramethylmu-cyclooctatetraene-diplatinum; 1, 2-diferrocenylethane,



$C_{22}H_{22}Fe_2$ ; 5-cyclooctadiene-cuprous chloride; dicyclopentadiene-cuprous chloride;  $C_{10}H_{12}CuCl$ ; bicycloheptadiene-cuprous chloride;  $C_7H_8CuCl$ ; dipentene-platinous chloride;  $C_{10}H_{16}PtCl_2$ ; dicyclopentadiene-platinous chloride; styrene-palladous chloride dimer  $(C_8H_8PdCl_2)_2$ ; and norbornadiene-palladous chloride,  $C_7H_8PdCl_2$ .

111. Jones, D., Pratt, L., and Wilkinson, G.,  $\pi$ -CYCLOHEXADIENYL COMPOUNDS OF MANGANESE, RHENIUM, IRON, AND RUTHERNIUM, Chemical Society Journal, 1962, p. 4458.

The interaction of salts of arene-metal cations with sodium borohydride or lithium aluminum hydride has given  $\pi$ -cyclohexadienyl derivatives of rhenium, iron, and ruthenium. In the case of ruthenium the isomer of the di- $\pi$ -cyclohexadienyl compound  $(\pi-C_6H_7)_2Ru$ , viz., benzene-cyclohexa-1, 3-dieneruthenium,  $C_6H_6RuC_6H_8$ , is also obtained. The interaction of phenyllithium with arene-metal salts gives 1-endo- $\pi$ -cyclohexadienyl derivatives such as  $\pi$ -(1-endo- $C_6H_5.C_6H_6$ ) $_2Ru$ .

The high-resolution nuclear magnetic resonance spectra of the compounds, and of  $\pi-C_6H_7Fe(CO)_3BF_4$ , have been measured and are discussed.

112. King, R. B. and Bisnette, M. B.,  $\pi$ -CYCLOPENTADIENYL- $\pi$ -INDENYLIRON, Angewandte Chemie, Vol. 75, No. 13, 1963, p. 642.

By the simultaneous action of the Na derivatives of indene and cyclopentadiene in tetrahydrofuran on  $FeCl_2$  was obtained up to 9 percent title compound (I), red-violet air-stable crystals, m.  $74-6^\circ$ . I was separated from simultaneously formed ferrocene by chromatography and fractional sublimation. Reduction of I over Pd-C (2 moles H absorbed) gave cyclopentadienyltetrahydroindenyliron, orange air-stable crystals, m.  $39-41^\circ$ .

113. Malakhov, V. I., Palitsyn, N. P., and Piskunova, E. M., FERROCENE, U. S. S. R. Patent 176,293 (Cl. C07f), 2 November 1965, Applied 8 October 1963, (Byul. Izobret. i Tovarnykh Znakov, No. 22, 1965, p. 28).

Ferrocene is prepared by reaction of anhydrous  $FeCl_2$ ,  $Et_2NH$ , and cyclopentadiene. The process is conducted in an

excess of  $\text{Et}_2\text{NH}$ , and the final product is recovered by steam distillation and is washed with boiling  $\text{H}_2\text{O}$ . The anhydrous  $\text{FeCl}_2$  is prepared by heating aqueous  $\text{FeCl}_2$  to  $160^\circ$  in vacuo.

114. Mitchell, C. D.,

FERROCENES FROM CYCLOPENTENONES, University Microfilms (Ann Arbor, Michigan), Order No. 64-2928, Dissertation Abstract, Vol. 24, No. 9, 1964, p. 3545.

The preparation of 3-cyclopentenone and 2, 5-dimethyl-3-cyclopentenone in approximately 30 percent yields by calcium acrylate and methacrylate pyrolyses has been reported elsewhere. In the present thesis a careful study of this reaction revealed that it gives, in fact, complex mixtures of products and is unsuitable for cyclopentenone synthesis. Gas-liquid chromatography of the distillate of the calcium acrylate pyrolyzate showed it to contain as many as 35 components with little evidence for the presence of 3-cyclopentenone. Examination of the calcium methacrylate pyrolyzate showed it to contain 2, 5-dimethyl-2-cyclopentenone and cis- and trans-2, 5-dimethylcyclopentanones, plus three other unidentifiable products. Pyrolysis of calcium cinnamate gave low yields of ethylbenzene, styrene and benzaldehyde plus as many as 15 other products.

The reaction of 3-methyl-2-cyclopentenone with sodium amide, than ferrous chloride, was reported earlier to give 1, 1'-dihydroxy-3, 3'-dimethylferrocene. This was confirmed in the present study and the following derivatives of the hydroxyferrocene were prepared: 1, 1'-dimethoxy-3, 3'-dimethylferrocene, cis-1, 1'-bis-((-)-methoxyacetoxy)-3, 3'-dimethylferrocene, trans-1, 1'-bis-((-)-menthoxyacetoxy)-3, 3'-dimethylferrocene, bis-(1, 1'-hydroxy-3, 3'-dimethylferrocene) diterephthalate, and 1, 1'-dihydroxy-3, 3'-dimethylferrocene diterephthalamate. Attempts to prepare 1, 1'-dihydroxy-3, 3'-dimethylferrocene disuccinate and 1, 1'-dihydroxy-3, 3'-dimethylferrocene diphthalate proved unsuccessful.

Optical resolution of the (-)-menthoxyacetoxy derivatives proved unsuccessful. However, hydrolysis of the bis-(1, 1'-dihydroxy-3, 3'-dimethylferrocene) diterephthalate showed it to have been selectively formed from D, L-1, 1'-dihydroxy-3, 3'-dimethylferrocene. The assignment of the racemic structure to the hydroxyferrocene was based upon the steric effects involved in the formation of the cyclic diterephthalate.

3-methyl-2-cyclopentenone also proved of value in the synthesis of alkylferrocenes. Reaction with ethyllithium and dehydration gave 1-ethyl-3-methylenecyclopentene, which could be converted to a mixture of cis- and trans-1, 1'-diethyl-3, 3'-dimethylferrocenes via initial isomerization of 3-ethyl-1-methylcyclopentadiene. Sodium amide was unsuccessful in effecting the isomerization, but sodium-potassium alloy proved effective. The synthesis of 1, 1'-diethyl-3, 3'-dimethylferrocene constitutes an independent proof of structure of 1, 1'-diacetyl-3, 3'-dimethylferrocene (obtained from acetylation of 1, 1'-dimethylferrocene), since the latter compound has been reduced to the tetraalkylferrocene; the two samples give identical infrared spectra.

Attempts to prepare other hydroxyferrocenes by the method described, from 2-cyclopentenone itself, from 2, 3, 4, 5-tetramethyl-2-cyclopentenone and from indanone, proved unsuccessful, although a number of bases (sodium amide in ammonia or toluene, sodium-potassium alloy, and potassium t-butoxide) were investigated.

115. Mock, W. and Richards, J. H.,  
SYNTHESIS OF BRIDGED FERROCENE DERIVATIVES WITH  
FUNCTIONAL GROUPS ON THE  $\beta$ -CARBON OF THE BRIDGE,  
Journal of Organic Chemistry, Vol. 27, 1962, pp. 4050-4051.

Dimethyl 1, 1'-ferrocene diacetate in 20 ml. dry  $\text{Et}_2\text{O}$  treated (N atm.) with about 2 moles 0.12 M  $\text{NaCPh}_3$  in  $\text{Et}_2\text{O}$  until the distinctive red color persisted and the mixture kept 4 hrs. at  $20^\circ$ , shaken with  $\text{H}_2\text{O}$  and the washed and dried  $\text{Et}_2\text{O}$  evaporated, chromatographed on silicic acid-Celite and eluted with  $\text{C}_6\text{H}_{14}\text{-CH}_2\text{Cl}_2$  yielded 85 percent orange needles of 1, 1'-( $\alpha$ -carbomethoxy- $\beta$ -oxotrimethylene) ferrocene (I), m.  $121.0\text{-}1.5^\circ$ . I (0.1 g.) in 20 ml.  $\text{H}_2\text{C:CMeOAc}$  containing 0.2 g. 4, 3-HO ( $\text{CO}_2\text{H}$ )  $\text{C}_6\text{H}_3\text{SO}_3\text{H}$  heated 6 hrs. at  $90^\circ$  and the cooled solution neutralized with aqueous  $\text{NaHCO}_3$ , extracted with  $\text{Et}_2\text{O}$  and the product chromatographed on silicic acid-Celite, eluted with  $\text{C}_6\text{H}_{14}\text{-CHCl}_3$  and recrystallized from  $\text{C}_7\text{H}_{16}$  yielded 75 percent I enol acetate,  $\text{C}_{17}\text{H}_{16}\text{FeO}_4$ , m.  $149\text{-}50^\circ$ , providing the first reported ferrocene derivative bridged by a 3 C chain including a double bond, and also supporting the suggestion that the case of effecting the Dieckmann cyclization is dependent on the planar nature of two of the bridging atoms including considerable mutual double bond character. I (0.25 g.) heated 30 min. at  $100^\circ$  in 20 ml.  $\text{AcOH}$

and 3 ml. concentrated HCl and the cooled solution adjusted to pH 8 with NaOH and  $\text{NaHCO}_3$ , extracted with  $\text{Et}_2\text{O}$  and the product chromatographed over silicic acid-Celite from  $\text{C}_6\text{H}_{14}\text{-CH}_2\text{Cl}_2$  yielded 85 percent 1, 1'-( $\beta$ -oxotrimethylene) ferrocene (II), m. 154-5°. II (52 mg.) in 15 ml. 2:1 AcOH-HCl kept 20 min. at 0° with 5 ml. MeSH and the mixture kept 20 min. at 0°, neutralized with NaOH and extracted with  $\text{Et}_2\text{O}$ , the product crystallized from  $\text{C}_8\text{H}_{18}$  and the orange crystals (m. 160-2°, 73 percent) refluxed 3 hrs. with stirring in absolute alcohol in the presence of W-5 Raney Ni, the filtered solution acidified and extracted with  $\text{Et}_2\text{O}$ , the residue on evaporation chromatographed from  $\text{C}_7\text{H}_{14}$  on neutral  $\text{Al}_2\text{O}_3$  (Merck) and the solid product sublimed at 64°/2 mm. gave 1, 1-trimethyleneferrocene, also obtained by Clemmensen reduction of 1, 1'-( $\alpha$ -oxotrimethylene) ferrocene (CA 51, 16442h).

116. Morehouse, E. L.,  
CYCLOPENTADIENYL-TYPE METALLIC COMPOUNDS,  
U. S. Patent 3,071,605 (Cl. 260-429), 1 January 1963,  
Applied 15 February 1955, 5 pp.

$\text{Et}_2\text{NH}$  (I) (175 ml.) was added to a suspension of 5 g. Fe and 0.083 mole  $\text{FeCl}_3$  in 175 ml.  $(\text{MeOCH}_2)_2$  and the mixture refluxed to form  $\text{FeCl}_2$ . Cyclopentadiene (II) (0.25 mole) was added to the cool solution, the mixture was warmed, cooled, and filtered, and the cake washed with petr. ether. The filtrate was vacuum stripped to yield 12.8 g. ferrocene (III). II (0.3 mole) was added to 0.1 mole  $\text{FeCl}_3$  in 170 ml. I, the mixture stirred for 6 hrs., 600 ml. petr. ether added, and the mixture treated as above to give 15.7 g. III. I (150 ml.) and 0.2 mole II were added to a mixture of 0.1 mole Br, 11.2 g. Fe, and 150 ml.  $(\text{MeOCH}_2)_2$  and the mixture was treated as above to yield 16.2 g. product. Methylcyclopentadiene (0.25 mole) was added to 0.125 mole  $\text{FeCl}_2$  in 150 ml.  $(\text{MeOCH}_2)_2$  and the mixture filtered. The filter cake was treated with HCl, amalgamated Zn added, the mixture extracted with  $\text{C}_6\text{H}_6$ , and the extract concentrated to yield  $\text{Fe}(\text{C}_5\text{H}_4\text{Me})_2$ . The powder resulting from grinding a cooled molten mixture of 0.085 mole Ni and 0.34 mole  $\text{Et}_2\text{NH.HCl}$  was added to 200 ml. I. II (0.17 mole) was added, the mixture filtered, and the filtrate and cake wash stripped to give 7.5 g.  $\text{Ni}(\text{C}_5\text{H}_5)_2$ .  $\text{ZrCl}_4$  (0.1 mole) was added to 0.25 mole II in 175 ml. I. After 5 hrs., 175 ml.  $\text{C}_6\text{H}_6$  was added, the mixture filtered, and the solution concentrated in vacuo to give 11.0 g.  $(\text{C}_5\text{H}_5)_2\text{ZrCl}_2$ .  $\text{TiCl}_4$  (0.125 mole) was added to 0.25 mole II

in 175 ml. I. To give  $(C_5H_5)_2TiCl_2$  and  $C_5H_5TiOCl$ . II (0.2 mole) was added to a mixture of 0.1 mole Br and 0.2 mole Co in 150 ml.  $(MeOCH_2)_2$ , 400 ml. petr. ether added, and the mixture concentrated in vacuo to give 12.5 g. Co  $(C_5H_5)_2$ .

117. Naval Air Station, Quonset Point, Rhode Island,  
RESEARCH ON ORGANIC CHEMISTRY AND FERROCENES  
by K. Schlogel, February 1962, Report No. ASD-TR-61-172,  
AD-274 691, Contract No. AF 61 (052)-383 (Unclassified  
Report).

Bridged ferrocenes were prepared by the following reaction-sequence: (A) formylation, (B) knoevenagel condensation, (C) cyclization of propionic acids (with trifluoroacetic anhydride), and (D) hydrogenation of cyclic ketones. A bistrimethylene and a diethyl-bistrimethylene ferrocene, the first twofold bridged ferrocenes, were obtained in this manner.

The latter represents the first hexasubstituted ferrocene prepared by substitution reactions starting from ferrocene itself. The stereochemistry of bridged ferrocenes was investigated by acetylation of the monobridged compound (trimethylene)-ferrocene, and the separation of stereoisomeric diacetyl derivatives was attempted. The diethyl compounds derived were synthesized independently. The stereochemical possibilities of bridged ferrocenes and the infrared data for elucidating the structure of stereoisomers are discussed. Ferrocenyl ethynylcarbinols were synthesized by the reaction of ferrocene aldehyde and acetylferrocene with sodium acetylide in liquid ammonia. The reaction of ferrocene aldehyde (or benzaldehyde) with carbinols lead to glycols. One of these glycols was also prepared by the reaction of dilithio acetylide with ferrocene aldehyde. Oxidative coupling of ferrocenylethynylcarbinols gave the corresponding diacetylenic glycols.

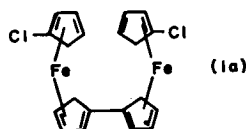
118. Nesmeyanov, A. N., Drozd, V. N., Sazonova, V. A.,  
Romanenko, V. I., Prokof'ev, A. K., and Nikonova, L. A.,  
BIFERROCENES AND TERFERROCENES, Translated from  
Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh  
Nauk, No. 4, 1963, pp. 667-674.

The preparation of biferrocenes and 1, 1'-diferrocenyl-ferrocene (1, 1'-terferrocene) is described by treating

1'-chloroferrocenecarboxylic acid with ammoniacal silver oxide. The velmann synthesis of polyferrocene was investigated.

119. Nesmeyanov, A. N., Drozd, V. N., Sazonova, V. A., Romanenko, V. I., Prokof'ev, A. K., and Nikonova, L. A., DIFFEROCENYLS AND TERFERROCENYLS, Izvestiya Akademii Nauk SSSR, Otdelnye Khimicheskikh Nauk, 1963, pp. 667-674.

Treatment of hot solution of 1- (1'-chloroferrocenyl) boronic acid with ammoniacal  $\text{AgNO}_3$  gave after extraction with  $\text{Et}_2\text{O}$  and purification on  $\text{Al}_2\text{O}_3$  22 percent bis [1- (1'-chloroferrocenyl)] (Ia), m.  $136.5-37^\circ$ , which also formed in 88 percent yield from 1'-chloro-1-iodoferrocene and Cu in 0.5 hr. at



$80-5^\circ$ . Cu and 1'-bromo-1-ethylferrocene in 0.5 hr. at  $125^\circ$  gave 100 percent bis [1- (1'-ethylferrocenyl)], m.  $96.5-97^\circ$ . Diferrocenyl stirred 2 hrs. with  $\text{AlCl}_3$  and  $\text{AcCl}$  in  $\text{CH}_2\text{Cl}_2$  gave after acidification 13.5 percent acetyldiferrocenyl, m.  $137.5-8.5^\circ$  and 46 percent bis [1- (1'-acetylferrocenyl)] (I), m.  $187-8^\circ$ . Separation on  $\text{Al}_2\text{O}_3$  by elution with  $\text{C}_6\text{H}_6$ , followed by  $\text{CHCl}_3-\text{C}_6\text{H}_6$ , elution with  $\text{CHCl}_3$  gave 6.2 percent triacetyldiferrocenyl, m.  $143-4^\circ$ . 1'-bromo-1-acetylferrocene and Cu in 24 hrs. at  $125^\circ$  gave 21.5 percent acetylferrocene and 54 percent I, m.  $188-8.5^\circ$ . Zn dust treated with  $\text{HgCl}_2$ -diluted  $\text{HCl}$  solution, followed by I in  $\text{AcOH}$ -concentrated  $\text{HCl}$  and refluxed 5 min. gave 43 percent bis [1- (1'-ethylferrocenyl)], m.  $93-4^\circ$ . Me 1'-bromoferrocene-1-carboxylate and Cu in 16 hrs. at  $125^\circ$  gave 14 percent Me ferrocenecarboxylate and 71.5 percent bis [1- (1'-carbomethoxyferrocenyl)], m.  $184-4.5^\circ$ . Heating bromoferrocene with 1, 1'-dibromoferrocene and Cu 15 min. at  $105^\circ$  and 45 min. at  $120^\circ$  (held 0.5 hr.) gave after chromatography on  $\text{Al}_2\text{O}_3$ : ferrocene, mixed haloferrocenes, 57 percent diferrocenyl, 14 percent 1, 1'-diferrocenylferrocene, m.

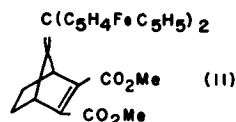
212.5-14.5° (sublimed in vacuo at 240° under N), and higher polyferrocenylenes, decomposed 260-5°, after reprecipitation from  $C_6H_6$  with petr. ether. Increased proportion of bromoferrocene in the reaction mixture gave up to 66.5 percent diferrocenyl.  $BzCH_2CH_2CO_2Et$  treated with dry  $EtONa$  under  $C_6H_6$  15 min., followed by acetylferrocene and kept 1 day, gave after an aqueous treatment and heating of the aqueous layer on a steam bath 21 percent red 3-ferrocenyl-1-phenylcyclopentadiene, m. 102-4°, which with  $NaNH_2$  in liquid  $NH_3$  2 hrs., followed by 12 hrs. in the presence of  $FeCl_3$  in xylene, gave 22 percent 1, 1'-diferrocenyl-3, 3'-diphenylferrocene, m. 232-3°. This reaction in the presence of cyclopentadiene gave 77 percent ferrocene, 15 percent 1-ferrocenyl-3-phenylferrocene, m. 172.5-73°, and 16.5 percent 1, 1'-diferrocenyl-3, 3'-diphenylferrocene. Infrared spectra of the products were reported; the bands at 1000 and 1113  $cm^{-1}$  were characteristic of two connected cyclopentadiene rings.

120. Nesmeyanov, A. N., Kritskaya, I. I., Rinehart, et. al., 1, 2-DIFERROCENYL-1, 2-DIPHENYLETHANE AND 1, 1-DIFERROCENYL-1, 2-DIPHENYLETHANE, Izvestiya Akademii Nauk SSSR, Otdeleniye Khimicheskiki Nauk, 1962, pp. 352-354 (cf. CA 50, 13886f, CA 53, 21856d).

The condensation product of  $CH_2O$  with ferrocene is 1, 2-diferrocenylethane, also prepared from ferrocene and  $(CH_2Cl)_2$  by the Friedel-Crafts method, m. 192.5°. Phenylferrocenylcarbinol treated with  $KHSO_4$  or  $SOCl_2$  yields the same mixture of products as formed from ferrocene and  $BzH$ ; these mixtures yielded products, m. 229-30° and 270-1°, diastereoisomeric 1, 2-diferrocenyl-1, 2-diphenylethanes. Clemmensen reduction of benzoylferrocene gave 49 percent benzylferrocene, m. 75-6°, and 41 percent benzoylphenyldiferrocenylmethane (I), m. 204-6°. Also formed was orange-red 1, 1'-diferrocenyl 1, 2-diphenylethane, m. 267-8°, which is also formed by reduction of I with  $LiAlH_4$ .

121. Nesmeyanov, A. N., Perevalova, E. G., Leont'eva, L. I., and Ustynyuk, Y. A.,  
TRIFERROCENYLCHLOROMETHANE HYDROCHLORIDE,  
Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya,  
No. 3, 1966, pp. 556-558 (In Russian).

Ferrocenyllithium from ferrocene and BuLi prepared in Et<sub>2</sub>O-tetrahydrofuran was treated with ferrocenecarboxaldehyde 1.5 hrs. at room temperature and gave after an aqueous treatment 62 percent diferrocenylcarbinol, m. 179-80° (under N), which with MnO<sub>2</sub> in CHCl<sub>3</sub> gave diferrocenyl ketone, 90 percent m. 209-10°. This and ferrocenyllithium gave 77 percent triferrocenylcarbinol, decomposed 200-1°. This and 71 percent HClO<sub>4</sub> in C<sub>6</sub>H<sub>6</sub>Et<sub>2</sub>O gave 96 percent green triferrocenylmethyl chloride perchlorate,



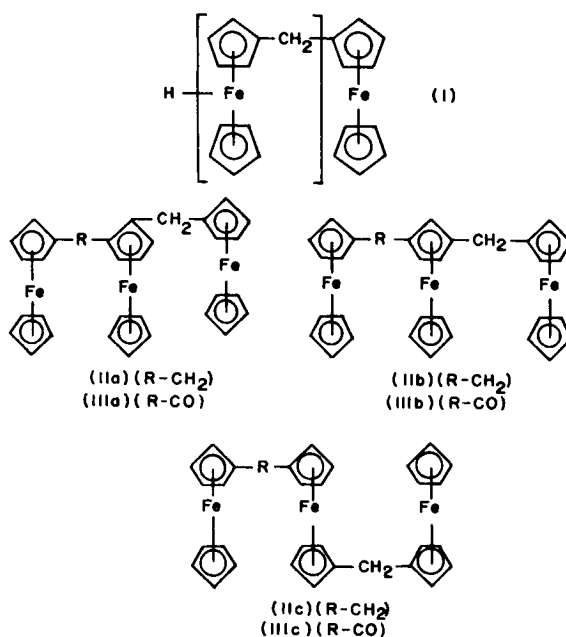
which exploded when heated; the carbinol and dry HCl in Et<sub>2</sub>O at 0° gave 97 percent green triferrocenylchloromethane-HCl which was storable for several days under N or in vacuo; its green solutions pass into red at room temperature. Treated with 5 percent HCl in MeOH this salt gave in 10 min. diferrocenylfulvene (I) red-violet, decomposed at 68-83°, which could not be purified satisfactorily, but was treated with Raney Ni in Et<sub>2</sub>O 5 hrs. at reflux to give 20 percent cyclopentylidiferrocenylmethane, m. 130-1.5°. I and (:CCO<sub>2</sub>Me)<sub>2</sub> kept 4 days in C<sub>6</sub>H<sub>6</sub> gave 7 percent II, orange-yellow, m. 189-90°.

122. Neuse, E. W., Quo, E., and Howells, W. G.,  
FERROCENE-CONTAINING POLYMERS. X. ISOMERIC  
BIS (FERROCENYLMETHYL) FERROCENES, Journal of  
Organic Chemistry, Vol. 30, No. 12, 1965, pp. 4071-4074  
(cf. CA 63, 8502c).

From a trinuclear fraction of the methylene-bridged ferrocene polymer I, obtained in earlier investigations, the isomeric 1, 2-, 1, 3-, and 1, 1'-bis (ferrocenylmethyl)



ferrocenes IIa-c are separated by fractional crystallization in the approximate ratio, 1:5:4. The three isomers are identified by elemental analyses and spectroscopic techniques. Their structural assignments are confirmed by independent synthesis via Clemmensen reduction of the corresponding



monoketones IIIa-c, obtained from ferrocenoyl chloride and diferrocenylmethane under Friedel-Crafts conditions. The established ratio of isomers II, while at best a very crude approximation, corroborates earlier qualitative predictions with regard to the sequence distribution of 1, 2-, 1, 3-, and 1, 1'-substituted recurring units along the backbone of polymer I.

123. Pauson, P. L. and Watts, W. E.,  
FERROCENE DERIVATIVES. PART XII. \* DI- AND  
TRI-FERROCENYLMETHANE DERIVATIVES, Chemical  
Society of England, Journal, 1962, p. 3880.

Diferrocenylmethane is obtained from ferrocene and paraformaldehyde. Its conversion via diferrocenyl ketone into a series of diferrocenylalkanols is described.  $\alpha$ -Diferrocenylbenzyl alcohol can also be obtained by condensation between ferrocene and benzoylferrocene. Two routes to

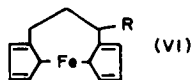
triferrocenylmethane and to 1, 1'-di (ferrocenylmethyl) ferrocene, a new method for preparing ferrocenecarboxyaldehyde, and the aldol condensation of acetylferrocene are reported.

124. Pruett, R. L. and Morehouse, E. L.,  
THE AMINE METHOD FOR PREPARING FERROCENE,  
Metal-Organic Compounds, Washington, D. C., American Chemical Society, No. 23, September 1959.

Ferrocene can be prepared on a laboratory or large-scale basis by the reaction of ferrous chloride and sodium cyclopentadienide in an amine solvent. The basicity of the latter is an important factor in the yield of ferrocene obtained. Other factors affecting the course of the reaction as well as the yield are discussed.

125. Rosenblum, M., Banerjee, A. K., Danieli, N., Fish, R. W., and Schlatter, V.,  
STRUCTURE AND CHEMISTRY OF FERROCENE. VII.  
BRIDGED FERROCENES, American Chemical Society Journal, Vol. 85, 1963, pp. 316-324 (cf. CA 57, 15149b).

Ferrocene (I) (11.16 g.) stirred 1 hr. at room temperature and 2 hrs. at 65-70° under N with 21.6 g. HCONMePh and 15.3 g. POCl<sub>3</sub>, the mixture cooled to 0°, and 50 g. NaOAc in 400 ml. H<sub>2</sub>O added to give, after purification through the bisulfite derivative, 10.2 g. formylferrocene (II) dark purple crystals, which, with malonic acid in C<sub>5</sub>H<sub>5</sub>N, gave 78 percent β-ferrocenylacrylic acid, 11 g. of which hydrogenated in absolute EtOH over PtO<sub>2</sub>, gave 10.3 g. β-ferrocenylpropionic acid (III), m. 119-20°. III (5.0 g.), stirred 5 hrs. at 0° under N with 7.5 g. (F<sub>3</sub>CCO)<sub>2</sub>O (IV) in 200 ml. CH<sub>2</sub>Cl<sub>2</sub>, gave 4.1 g. α-oxo-1, 1'-trimethyleneferrocene (V), m. 148-50° (petr. ether). V was reduced in four ways: 2 g. V, refluxed 5 hrs. under N with 0.364 g. NH<sub>2</sub>NH<sub>2</sub> and 5.5 g. NaOH in 50 ml. (HOCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>O, gave 1.4 g. VI (R = H) (VII), m. 108-9° (sublimation); V hydrogenated over PtO<sub>2</sub> in EtOH containing a little HCl, gave as



much as 89 percent crude VII, but also some VI ( $R = OH$ ) (VIII), and the symmetrical ether (IX) of VIII; V (450 mg.) refluxed 4 hrs. under N with Zn-Hg in EtOH- $C_6H_6$ -concentrated HCl, gave 400 mg. impure VII; and 5 g. V refluxed 5 hrs. with 5 g.  $LiAlH_4$  in 200 ml. anhydrous  $Et_2O$  gave 4.65 g. VIII, yellow needles, m.  $163-4^\circ$  ( $Et_2O$ ). VII (1.36 g.) treated 3 hrs. at  $0^\circ$  under N with 0.47 g.  $AcCl$  and 0.80 g.  $AlCl_3$  in dry  $CH_2Cl_2$ , the mixture poured into ice- $H_2O$ , the oily residue obtained on work-up chromatographed on  $Al_2O_3$  and eluted with petr. ether- $C_6H_6$  gave 200 mg. VII, 370 mg. 2-acetyl-1, 1'-trimethyleneferrocene, m.  $77.5-8.5^\circ$  (petr. ether), and 610 mg. 3-acetyl-1, 1'-trimethyleneferrocene, m.  $103-4^\circ$  (petr. ether). V (4 g.) in 150 ml. absolute MeOH, kept 72 hrs. in the dark with 125 ml.  $Et_2O$  containing 0.018 mole  $CH_2N_2$ , HOAc added, and the solvent removed, gave after chromatography on  $Al_2O_3$ , and elution with petr. ether and petr. ether  $Et_2O$  2.25 g.  $\beta$ -oxo-1, 1'-tetramethyleneferrocene (X), m.  $113.5-14.5^\circ$ , 1.3 g. V, and a small amount of  $\alpha$ -oxo-1, 1'-tetramethyleneferrocene (XI), m.  $101-2^\circ$ . X (800 mg.), reduced with  $NH_2NH_2$  as was V, gave 600 mg. 1, 1'-tetramethyleneferrocene (XII), m.  $63-4^\circ$ . It was much easier to introduce a double bond into a  $C_4$ -bridged ferrocene than into a  $C_3$  system. Thus, 193.4 mg. X, refluxed 48 hrs. under N with 38.7 mg.  $p-MeC_6H_4SO_3H$  and 30 ml. freshly distilled  $AcOCMe:CH_2$  (XIII), excess XIII removed in vacuo, the orange-brown residue dissolved in 200 ml.  $Et_2O$ , the solution washed three times with 1 percent  $NaHCO_3$  and six times with  $H_2O$ , dried with  $MgSO_4$ , the solvent removed in vacuo, the residue [in Skellysolve B (XIV)] chromatographed on Florisil and eluted with  $Et_2O$ -petr. ether (1:9 and 1:1), gave 45.5 mg. the enol acetate (XV), yellow needles, m.  $123-4^\circ$ , of X, and 147.3 mg. X. Similarly, V gave 7-10 percent its orange enol acetate (XVI), m.  $129-30^\circ$ . Acetylferrocene, similarly treated, gave 25 percent its orange enol acetate (XVII), m.  $50.5-51^\circ$ . X exchanged with  $D_2O$  and  $NaOMe$ , while V did not. V was recovered unchanged on treatment with  $Me_3COK$  and  $MeI$ . Attempts to convert VIII into an olefin were not successful. Thus, distillation of VIII from  $KHSO_4$  gave only IX, and pyrolysis of the  $p$ -nitrobenzoate and xanthate of VIII did not give olefin. VIII (2.5 g.) stirred 6 hrs. at  $0^\circ$  with 10 ml.  $ClCO_2Et$  in 25 ml.  $C_5H_5N$ , and the mixture poured into

ice-H<sub>2</sub>O, gave 2.35 g. VI (R = OCO<sub>2</sub>Et) (XVIII), yellow plates, m. 120-1° (CH<sub>2</sub>Cl<sub>2</sub>-petr. ether). Similarly, VIII with ClCO<sub>2</sub>Me gave 66 percent VI (R = OCO<sub>2</sub>Me) (XIX), yellow blocks, m. 143-4° (Et<sub>2</sub>O-petr. ether). XVIII (1 g.) in 10 ml. of dry xylene, dropped in a slow stream of N through a tube packed with alundum chips at 283°, the tube washed with Et<sub>2</sub>O, the Et<sub>2</sub>O removed, the xylene solution chromatographed on wet Al<sub>2</sub>O<sub>3</sub> and eluted with petr. ether, gave no olefin, but 300 mg. VI (R = OEt) (XX), yellow needles, m. 46-7° (sublimation), 122 mg. IX, m. 229-30° (CH<sub>2</sub>Cl<sub>2</sub>-petr. ether), and 46 mg. VIII. XIX (500 mg.), similarly pyrolyzed, gave 281 mg. VI (R = OMe) (XXI), orange blocks, m. 57.5-8.5° (petr. ether), 32 mg. IX, and 11 mg. VIII. VIII (250 mg.) with five drops 70 percent HClO<sub>4</sub> in 20 ml. EtOH, gave 294 mg. XX. Similarly, 250 mg. VIII in MeOH gave 242 mg. XXI. XX was also formed by heating VIII in aqueous EtOH containing a trace of HOAc. I (5 g.) stirred overnight with 5 g. freshly distilled Me<sub>2</sub>C (COCl)<sub>2</sub> in CH<sub>2</sub>Cl<sub>2</sub>, ice-H<sub>2</sub>O added, the organic layer washed with Na<sub>2</sub>CO<sub>3</sub> solution and H<sub>2</sub>O, dried over MgSO<sub>4</sub>, the solvent removed, the residue taken up in XIV, chromatographed on wet Al<sub>2</sub>O<sub>3</sub>, and eluted with C<sub>6</sub>H<sub>6</sub>-XIV, gave isobutyrylferrocene, yellow oil, 1, 1'-diisobutyrylferrocene, yellow-orange plates, m. 50-1°, and dimethyldiferrocenylnmethane, orange needles, m. 141-2° (petr. ether). Freshly sublimed II (15 g.) refluxed 20 min. with 38 g. Me<sub>2</sub>CBrCO<sub>2</sub>Et and Mg-Hg in 450 ml. anhydrous Et<sub>2</sub>O, the mixture decomposed with ice and 200 ml. 10 percent H<sub>2</sub>SO<sub>4</sub>, and worked up gave 22.5 g. crude Et α, α-dimethyl-β-hydroxy-β-ferrocenylpropionate, yellow oil, which was hydrogenated over 900 mg. PtO<sub>2</sub> in 150 ml. glacial HOAc containing 1.5 ml. 70 percent HClO<sub>4</sub> to give 19.5 g. Et α, α-dimethyl-β-ferrocenylpropionate (XXII); yellow oil. XXII (5 g.) refluxed 4 hrs. under N with 200 ml. MeOH containing 10 g. KOH, and the mixture poured into H<sub>2</sub>O, gave 2.94 g. α, α-dimethyl-β-ferrocenylpropionic acid (XXIII), m. 143-7° (Et<sub>2</sub>O-petr. ether). XXIII (3.0 g.), treated with IV as was III (although more vigorous conditions were required), gave, after chromatography on Al<sub>2</sub>O<sub>3</sub> and elution with petr. ether-Et<sub>2</sub>O, 1.2 g. α-oxo-β, β-dimethyl 1, 1'-trimethyleneferrocene (XXIV), m. 134-5° (Et<sub>2</sub>O-petr. ether), and 1.1 g. α-oxo-β, β-dimethyl-1, 2-trimethyleneferrocene, orange oil. XXIV (1.8 g.), hydrogenated at 27 lbs. over 200 mg. PtO<sub>2</sub> in 200 ml. glacial HOAc containing 2 ml. 70 percent HClO<sub>4</sub> gave, after chromatography on wet Al<sub>2</sub>O<sub>3</sub> and elution

with petr. ether, 1.4 g.  $\beta$ ,  $\beta$ -dimethyl-1, 1'-trimethylene-ferrocene (XXV), m. 98-101° (petr. ether). Conversion of XXIV to XXV proceeded poorly with  $\text{NH}_2\text{NH}_2$ . 1, 1': 3, 3'-bis (trimethylene) ferrocene (XXVI) was prepared as by Schloegl and Seiler (CA 54, 21024h). Nuclear magnetic resonance spectra were given for VII, XII, XV, XVI, XXV, and XXVI. Ultraviolet (UV) spectra were given for 95 percent EtOH solutions of V, VII, X, XI, XV, XVI, XVII, XXIV (in isooctane), 1-acetyl-1'-ethylferrocene, and 1, 1'-diethylferrocene. The conformation of bridged ferrocene compounds, in particular the coplanarity of the rings, was discussed, with evidence from nuclear magnetic resonance, ultraviolet, and infrared spectra used to deduce conformations.

126. Royal Aircraft Establishment, Farnborough, England, DIFERROCENYL by O. A. Nesneyanova and E. G. Perevalova, AD-230 058 (Unclassified Report).

Not abstracted.

127. Royal College of Science and Technology, Glasgow, Scotland, SOME SUBSTITUTED CYCLOPENTADIENYL DERIVATIVES OF NICKEL, COBALT, IRON, MOLYBDENUM, AND TITANIUM by G. R. Knox, J. D. Munro, P. L. Pauson, G. H. Smith, and W. E. Watts, April 1961, Report No. AFOSR-2027, AD-613 753, Contract No. AF 61 (052)-321 (Unclassified Report) (Chemical Society Journal (Great Britain), No. 904, October 1961, pp. 4619-4624).

The applicability to other transition metals of methods developed for the synthesis of ferrocenes is demonstrated. The extension of the fulvene synthesis to aminofulvenes is described.

128. Schlogel, K. and Peterlik, M., FERROCENE DERIVATIVES. X. SYNTHESIS OF A 4-FOLD BRIDGED FERROCENE, Tetrahedron Letters, 1962, pp. 573-576 (In German) (cf. CA 57, 3481b).

The formerly described bis (trimethylene) ferrocene (I) was systematically converted by introduction of further trimethylene bridges to tris (trimethylene) ferrocene (II) and tetrakis (trimethylene) ferrocene (III). Treatment of

ferrocene-1, 1'-bis (propionyl chloride) in very dilute solution with  $\text{AlCl}_3$  gave the heteroannular diketone,  $\text{C}_{16}\text{H}_{14}\text{FeO}_2$ , m.  $210^\circ$ , smoothly converted with  $\text{LiAlH}_4\text{-AlCl}_3$  to yield 15 percent I. As a model compound a highly substituted ferrocene was prepared. Alternating Friedel-Crafts acetylation and reduction with  $\text{LiAlH}_4\text{-AlCl}_3$  gave decaethylferrocene (IV),  $\text{C}_{30}\text{H}_{50}\text{Fe}$ , m.  $210\text{-}30^\circ$  (decomposition). As a result of increasing symmetry and decreasing isomerization the lower homologs are liquid and with increasing substitution show decreasing  $n_D$  and increasing  $R_F$  values (thin layer chromatography on silica gel G in  $\text{C}_6\text{H}_{14}$ ). The intensity of the characteristic Fe-H band in the infrared diminishes with simultaneous shift to longer wavelength ( $3090\text{-}3040\text{ cm}^{-1}$ ) with increasing substitution, vanishing entirely with IV. IV similarly loses the characteristic ring proton signal at  $5.8\text{-}6.0\tau$  in the nuclear magnetic resonance spectrum. Accordingly two further heteroannular rings were introduced into I by use of the formerly described procedures. The three-fold bridged ketone was separated into two isomers, m.  $159\text{-}60^\circ$ , and m.  $185\text{-}8^\circ$ , reduced with  $\text{LiAlH}_4\text{-AlCl}_3$  to the isomeric II, m.  $156\text{-}60^\circ$ , and m.  $150\text{-}5^\circ$ . The  $156\text{-}60^\circ$ -isomer, assigned the 1, 2, 4-structure, was successively converted to the aldehyde, m.  $109\text{-}13^\circ$ ; the acrylic acid analog, m.  $150\text{-}60^\circ$ ; propionic acid analog, m.  $160^\circ$ , and to the ring ketone, m.  $175\text{-}80^\circ$ , finally reduced to the crystalline, chromatographically unique III, m.  $159\text{-}62^\circ$ , in 4-mg. yield from 25 g. ferrocene. The series I, II, III, similarly to the increasingly substituted ferrocene series showed a steady diminution of the intensity of the Fe-H band with simultaneous shift from  $3090$  to  $3040\text{ cm}^{-1}$  in the infrared spectrum.

129. Schlogel, K. and Seiler, H.,  
A DOUBLY BRIDGED FERROCENE (Foreign title not available), Translated into English from the German by U. S. Army Missile Command, Redstone Arsenal, Alabama, Report No. RSIC-542 (Tetrahedron Letters, Vol. 7, 1960, pp. 4-8).

So far, only those representatives of bridged ferrocenes have been known in which the (heteroannular) linking of the two cyclopentadiene rings occurs by means of a single carbon chain. Such compounds could be prepared by intramolecular

acylation (bridges consisting of three carbon atoms), or via  $\alpha$ ,  $\omega$ -bis-cyclopentadienyl alkanes (bridges consisting of 3-5 carbon atoms), or through acyloin ring closure of ferrocene-1, 1'-bis-fatty acid esters (bridge containing 4-10 C atoms).

Starting from  $\beta$ -ferrocenylpropionic acid methyl ester (I) which was obtained from the corresponding acid with diazomethane, from ferrocene-1, 1'-bis-propionic acid (V) or also from singly bridged ferrocene (VIII) the doubly-bridged compound bis- (trimethylene)-ferrocene (XIII) was prepared. Regardless of which of the three starting materials is used, the same key substance, the bridged ketone (XII), is always obtained.

130. Schlogel, K., Peterlik, M., and Seiler, H.,  
FERROCENE DERIVATIVES. XII. MULTI-BRIDGED  
FERROCENES. 1. SYNTHESIS OF BISTRIMETHYLENE-  
FERROCENE, XIII. MULTI-BRIDGED FERROCENES, 2.  
TRIS- AND TETRAKISTRIMETHYLENEFERROCENE,  
Monatshefte, Vol. 93, 1962, pp. 1309-1342.

## XII

1, 1': 3, 3'-bis (trimethylene) ferrocene (I) was prepared (a) from 1, 1'-trimethyleneferrocene (II) by formylation, condensation with  $\text{CH}_2(\text{CO}_2\text{H})_2$ , hydrogenation, cyclization, and reduction; and (b) (the better method) from 1, 1'-bis ( $\beta$ -carboxyethyl) ferrocene (III) via the bis (acid chloride) (IV) through a Friedel-Crafts cyclization, followed by reduction. The structure of I was based on infrared data and on the expected predominance of 1, 3- over 1, 2-isomers from formylation or acylation of alkylferrocenes. 1, 2-isomers were usually not removed until final purification of solid di-bridged compounds. For steric reasons, 1, 2:1', 3'-dibridging was not considered likely. Cyclization of 1, 3 (?) -bis ( $\beta$ -carboxyethyl) ferrocene (V) produced only one bridge, and subsequent homoannular cyclization did not occur owing to deactivation of one ring by an acyl group on the other. For the same reason, 1-acetyl-1'- ( $\beta$ -carboxyethyl) ferrocene (VI) failed to yield a cyclic ketone either with  $(\text{CF}_3\text{CO})_2\text{O}$  or in a Friedel-Crafts reaction. Acetylation of II followed by reduction gave mainly two isomeric diethyl-1, 1'-trimethyleneferrocenes, identical with two isomers obtained by bridging 1, 1'-diethylferrocene (VII) via formylated

VII.  $\beta$ -Ferrocenylpropionic acid (VIII) in  $\text{Et}_2\text{O}$  with  $\text{CH}_2\text{N}_2$  gave 92 percent Me ester (IX),  $b_{0.5}$   $120-5^\circ$  (bath temperature throughout this abstract), m.  $36-8^\circ$  (petr. ether). Similarly, 1-acetyl-1'-carboxyferrocene yielded 82 percent Me ester (X), m.  $101-2^\circ$  ( $\text{C}_6\text{H}_6$ -petr. ether). X (1.7 g.) in 50 ml. absolute tetrahydrofuran was added dropwise to 0.46 g.  $\text{LiAlH}_4$  in 50 ml. refluxing tetrahydrofuran, the mixture refluxed 1 hr., decomposed with  $\text{H}_2\text{O}$ , filtered, and the solution evaporated at  $25^\circ/10$  mm. to give 1.5 g. crude 1-( $\alpha$ -hydroxyethyl)-1'-hydroxymethylferrocene (XI). XI (1.5 g.) and 3.0 g. activated  $\text{MnO}_2$  in 15 ml.  $\text{CHCl}_3$  was kept 3 days with occasional shaking, filtered, the solid washed with  $\text{CHCl}_3$ , solvent removed from the filtrate, the residue crystallized ( $\text{C}_6\text{H}_6$ -petr. ether), and the filtrate chromatographed on  $\text{Al}_2\text{O}_3$  to give 64 percent 1-acetyl-1'-formylferrocene (XII), m.  $90-3^\circ$ ; disemicarbazone, m.  $243^\circ$ .  $\text{POCl}_3$  and  $\text{PhMeNCHO}$  (0.02 mole each) was stirred 1 hr. at room temperature, 0.01 mole ferrocene derivative in 20 ml. absolute  $\text{CH}_2\text{Cl}_2$  added in 15 min., the mixture stirred until homogeneous, kept 72 hrs. in the dark at room temperature, poured on ice, some  $\text{Na}_2\text{S}_2\text{O}_4$  added after 1 hr., the aqueous phase extracted with  $\text{CH}_2\text{Cl}_2$ , the combined organic layers washed with aqueous  $\text{NaHCO}_3$  and  $\text{H}_2\text{O}$ , dried, solvent removed, the  $\text{PhMeNCHO}$  and  $\text{PhMeNH}$  removed at 0.5 mm., and the formyl compound purified by distillation or chromatography on  $\text{Al}_2\text{O}_3$  (ferrocene derivative, purification, percent yield, and aldehyde given): ethylferrocene, distillation ( $b_{0.2}$   $90-110^\circ$ ), 58, 1-ethyl-3(?) -formylferrocene (XIII); IX,  $\text{Al}_2\text{O}_3$  and distillation ( $b_{0.5}$   $160-70^\circ$ ), 65, 1-( $\beta$ -carbo-methoxyethyl)-3(?) -formylferrocene (XIV) [semicarbazone m.  $116-20^\circ$  ( $\text{Et}_2\text{O}$ -petr. ether)]; II,  $\text{Al}_2\text{O}_3$ , 60, 1, 1'-trimethylene-3(?) -formylferrocene (XV); VII,  $\text{Al}_2\text{O}_3$  and distillation ( $b_{1.5}$   $150-60^\circ$ ), 70, 1, 1'-diethyl-3(?) -formylferrocene (XVI) [semicarbazone m.  $116-20^\circ$  ( $\text{EtOH-H}_2\text{O}$ )]. The aldehyde (0.01 mole) and 0.02 mole  $\text{CH}_2(\text{CO}_2\text{H})_2$  in 30 ml. absolute pyridine was treated with 0.1 ml. piperidine, the mixture heated 2 hrs. on a water-bath, solvent removed in vacuo, the residue kept 15 min. at 10 mm. at  $100^\circ$ , dissolved in  $\text{EtOH}$ , the solution carefully acidified with concentrated  $\text{HCl}$ , and the mixture diluted with  $\text{H}_2\text{O}$  to precipitate the carboxyvinyl compound, usually containing some unsaturated malonic acid [aldehyde, product, percent yield, melting point, recrystallization solvent, and  $R_f$  value (CA 54,



21024h) given]: XIV, 1-( $\beta$ -carboxyethyl)-3(?)-( $\beta$ -carboxyvinyl) ferrocene (XVII), 65, 147-50°, MeOH-H<sub>2</sub>O, 0.35; XV, 1, 1'-trimethylene-3(?)-( $\beta$ -carboxyvinyl) ferrocene (XVIII), 23, 150-5°, MeOH-H<sub>2</sub>O, 0.70; XII, 1-acetyl-1'-( $\beta$ -carboxyvinyl) ferrocene (XIX), 64, 158-60° (decomposition), —, 0.49; XVI, 1, 1'-diethyl-3(?)-( $\beta$ -carboxyvinyl) ferrocene (XX), 95, —, —, 0.71. In the isolation of XVII and XIX, the pyridine was removed, the residue dissolved in CHCl<sub>3</sub> or CH<sub>2</sub>Cl<sub>2</sub>, and the solution extracted with N NaOH. Hydrogenation of the carboxyvinyl compounds (0.01 mole) in 30 ml. EtOH with 0.1 g. 10 percent Pd-C, filtration, evaporation in vacuo, and crystallization of the residue (EtOH-H<sub>2</sub>O) or (if paper chromatography showed the malonic acid was present) distillation at 0.1 mm. gave the carboxyethyl compound (carboxyvinyl compound, carboxyethyl compound, yield, melting point and R<sub>f</sub> value given): XVII, V; almost quantitative, —, 0.38; XVIII, 1, 1'-trimethylene-3(?)-( $\beta$ -carboxyethyl) ferrocene (XXI), 70-90 percent, —, 0.71; XIX, VI, almost quantitative, 65-70° (CH<sub>2</sub>Cl<sub>2</sub>-petr. ether), 0.50; XX, 1, 1'-diethyl-3(?)-( $\beta$ -carboxyethyl) ferrocene (XXII), 86 percent, b<sub>0.05</sub> 120-30°, 0.60. The carboxyethyl compound (0.001 mole) was added gradually to 3-5 ml. ice-cold (CF<sub>3</sub>CO)<sub>2</sub>O (in CCl<sub>4</sub>, if necessary), the mixture kept overnight at 0°, poured on ice, stirred 1 hr., extracted thoroughly with CH<sub>2</sub>Cl<sub>2</sub>, the extract washed with aqueous NaHCO<sub>3</sub> and H<sub>2</sub>O, dried, solvent removed, and the residue chromatographed on Al<sub>2</sub>O<sub>2</sub> to give the cyclic ketone (propionic acid, additional purification, product, percent yield, melting point, and R<sub>f</sub> value given): V, —, 1', 1-( $\alpha$ -oxotrimethylene)-3(?)-( $\beta$ -carboxyethyl) ferrocene (XXIII), 80 percent, —, 0.56; XXI, —, 1, 1'-trimethylene-3, 3'-( $\alpha$ -oxotrimethylene) ferrocene (XXIV), 71 percent, 110-13° (MeOH-H<sub>2</sub>O)—; XXII, distillation (b<sub>0.05</sub> 140-50°)-acid Al<sub>2</sub>O<sub>3</sub>-distillation, 1, 2, 1', 2'-diethyl-( $\alpha$ -oxotrimethylene) ferrocene (XXV) and 1, 3, 1', 3'-diethyl-( $\alpha$ -oxotrimethylene) ferrocene (XXVI) (ratio 1:7) (and a small amount of the 1, 2, 1', 31-isomer), 44 percent, —, —. Cyclic ketones were reduced either by H-PtO<sub>2</sub> in AcOH or with LiAlH<sub>4</sub>-AlCl<sub>3</sub> in Et<sub>2</sub>O or tetrahydrofuran (CA 56, 15545h); the latter method gave high yields of trimethylene compounds, which were purified by chromatography on Al<sub>2</sub>O<sub>3</sub>, distillation at 0.1 mm., and crystallization from EtOH-H<sub>2</sub>O. Reduction of XXIV by either method gave almost quantitative I. Reduction of XXV and XXVI separately with LiAlH<sub>4</sub>-AlCl<sub>3</sub> and distillation (b<sub>0.05</sub> 90-100°) gave 1, 2, 1', 2'-diethyltrimethyleneferrocene (XXVII) and 1, 3, 1'-3'-diethyltrimethyleneferrocene

(XXVIII), respectively. 1, 1'-diacetylferrocene (XXIX) (13.3 g.) was added in portions to  $\text{NaNH}_2$  from 4.7 g. Na and 200 ml. liquid  $\text{NH}_3$ , the mixture stirred 1 hr., 200 ml. absolute  $\text{Et}_2\text{O}$  added,  $\text{NH}_3$  removed, and the mixture refluxed while 48.0 g.  $(\text{EtO})_2\text{CO}$  in 100 ml. absolute  $\text{Et}_2\text{O}$  was added dropwise. After 2 hrs. reflux and 2 hrs. at room temperature, the mixture was filtered, the solid Na-salt washed with  $\text{Et}_2\text{O}$ , the filtrate freed of excess  $(\text{EtO})_2\text{CO}$  in vacuo, the residue and the Na-salt combined under  $\text{Et}_2\text{O}$ , the mixture treated carefully with ice-cold 1N  $\text{HCl}$ , the  $\text{Et}_2\text{O}$  washed with  $\text{H}_2\text{O}$ , dried, and evaporated to give 90 percent crude 1, 1'-bis-( $\alpha$ -oxo- $\beta$ -carbethoxyethyl) ferrocene (XXX). XXX (18.2 g.) in 200 ml.  $\text{AcOH}$  with H and  $\text{PtO}_2$  (0.5 g. initially, 1.0 g. total) for 3 days, the crude ester isolated, heated 4 hrs. in 100 ml. N  $\text{NaOH}$  and 110 ml.  $\text{EtOH}$ , the  $\text{EtOH}$  removed in vacuo,  $\text{H}_2\text{O}$  added, the ester extracted with  $\text{Et}_2\text{O}$ , the aqueous layer acidified, extracted with  $\text{Et}_2\text{O}$ , and the extract evaporated gave 78 percent (based on XXIX) III, m.  $142-5^\circ$ ,  $R_f$  0.38.  $\text{PCl}_3$  (150 ml.) and 8.4 g. III stirred 2.5 hrs. at room temperature, excess  $\text{PCl}_3$  removed at  $20^\circ$  in vacuo, 170 ml. absolute  $\text{CH}_2\text{Cl}_2$  added, and the solution decanted gave a solution of IV. The solution was added dropwise with vigorous stirring to 14.0 g.  $\text{AlCl}_3$  in 1 l.  $\text{CH}_2\text{Cl}_2$  during 1.5 hrs. in an ice bath and 1.5 hrs. at reflux, the mixture was refluxed in 3 hrs., added to ice, the mixture stirred 1 hr., treated with  $\text{Na}_2\text{S}_2\text{O}_4$ , the organic phase and extracts washed with  $\text{NaHCO}_3$  and  $\text{H}_2\text{O}$ . solvent removed, the residue extracted with  $\text{C}_6\text{H}_6$ , and the extract chromatographed on  $\text{Al}_2\text{O}_3$  to give 37 percent 1, 1', 3', 3'-bis ( $\alpha$ -oxotrimethylene) ferrocene (XXXI), m.  $206-10^\circ$  ( $\text{C}_6\text{H}_6$ -petr. ether). XXXI (2.8 g.) reduced with  $\text{LiAlH}_4$ - $\text{AlCl}_3$  in tetrahydrofuran gave 69 percent I, m.  $88-91^\circ$  ( $\text{MeOH-H}_2\text{O}$ ) after sublimation ( $b_0$ . 80- $100^\circ$ ). III treated with  $(\text{CF}_3\text{CO})_2\text{O}$  as above yielded 80 percent 1, 1'-( $\alpha$ -oxotrimethylene)-3 (?)-( $\beta$ -carboxyethyl) ferrocene (XXXII),  $R_f$  0.56. Reduction of either XXXII or XXXIII with H- $\text{PtO}_2$  in  $\text{AcOH}$  gave 70-90 percent XXI. II (0.95 g.) in 40 ml. absolute  $\text{CH}_2\text{Cl}_2$  was added to 0.98 g.  $\text{AcCl}$  and 1.73 g.  $\text{AlCl}_3$  in 25 ml.  $\text{CH}_2\text{Cl}_2$  during 30 min., the mixture stirred 4 hrs., refluxed 1 hr., cooled poured on ice, the organic layer and two extracts shaken with aqueous  $\text{NaHCO}_3$  and  $\text{H}_2\text{O}$ , chromatographed on acidic  $\text{Al}_2\text{O}_3$ , and the main fractions crystallized from petr. ether to give (in the order eluted) 0.009 g. 1, 2, 1', 3'-diacetyltrimethyleneferrocene, m.  $139-46^\circ$ , 0.32 g. 1, 2, 1', 2'-diacetyltrimethyleneferrocene (XXXIII), m.  $111-15^\circ$ , and 0.50 g. 1, 3, 1', 3'-diacetyltrimethyleneferrocene (XXXIV), m.  $134-6^\circ$  (apparently each a mixture of cis

and trans forms). Reduction of XXXIII and XXXIV with  $\text{LiAlH}_4$ - $\text{AlCl}_3$  or  $\text{H-PtO}_2$  gave XXVII and XXVIII, respectively,  $b_{0.05}$  90-100° (infrared comparison). XIII (0.6 g.) and 0.1 g.  $\text{LiAlH}_4$  heated 1 hr. in  $\text{Et}_2\text{O}$  gave 96 percent 1-ethyl-3 (?) -hydroxymethylferrocene (XXXV),  $b_{0.2}$  130-40°. Similarly, XIV yielded almost quantitative 1- ( $\gamma$ -hydroxypropyl)-3 (?) -hydroxymethylferrocene (XXXVI),  $b_{0.5}$  180-90°. X (0.011 mole) in 70 ml. absolute  $\text{Et}_2\text{O}$  added dropwise to 0.011 mole  $\text{LiAlH}_4$  in 50 ml.  $\text{Et}_2\text{O}$ , stirred 1 hr. at room temperature, worked up as in the preparation of XI, and the crude product chromatographed on  $\text{Al}_2\text{O}_3$  gave 16 percent 1- ( $\alpha$ -hydroxyethyl)-1'-carbomethoxyferrocene and 83 percent 1, 1'- ( $\alpha$ -methyl dimethyleneoxy) ferrocene, m. 55-9° after thin-layer chromatography. Structures for XXXIII, XXXIV, XXV, and XXVI were based in part on yield ratios and order of elution in chromatography. Loss of coplanarity between the CO group and the ring in XXIV and XXXI was evident from low  $\epsilon$ -values for ultraviolet absorption maximum. Unlike maximums for certain non-bridged oxoferrocenes, maximum for XXXIII and XXXIV were not helpful in a choice between a 1, 2- and a 1, 3-structure. Maximums for XXIX were given. In accordance with known rules for 1, 3-versus 1, 2-isomers, the dibridged ketones showed bands in the infrared at 905 and 925  $\text{cm.}^{-1}$  (XXXI) or 905 and 930  $\text{cm.}^{-1}$  (XXIV), as did XXXIV; XXXIII had no band at 905  $\text{cm.}^{-1}$ ; and I had a doublet at 911 and 936  $\text{cm.}^{-1}$ . Bands at 1105 and 1000  $\text{cm.}^{-1}$  (unsubstituted ring) were shown by XIII, XIV, XXXV, and XXXVI. Mass spectral data were given for I and II. The structure of I as written earlier (CA 57, 15151a) was misinterpreted by Rosenblum, et al. (CA 57, 12533a); from models, the two bridges can be bound only to C atoms lying over one another.

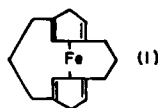
### XIII

The formylation sequence used to prepare I was applied to I to give 1, 1': 2, 2': 3, 3' - (XXXVII) and 1, 1': 2, 2': 4, 4' - tris (trimethylene) ferrocene (XXXVIII) and was then applied to XXXVIII to give tetrakis (trimethylene) ferrocene (XXXIX). As model compounds, 1, 1'-diethyl-3, 3': 4, 4' (?) - bis (trimethylene) ferrocene (XL) was similarly prepared from XXII Me ester (XLI), and decaethylferrocene (XLII) was prepared from VII by repeated acetylation-reductions. With increasing substitution on ferrocene, infrared absorption

bands at 3040-3090  $\text{cm.}^{-1}$  (aromatic C-H) decreased in wave number and intensity and were characteristic of the degree of substitution [number of substituents and wave number ( $\text{cm.}^{-1}$ ) given]: 0, 3090; 2, 3085; 4, 3075; 5, 3070; 6, 3060-65; 7, 3050; 8, 3040; 10, (no band). Determination of formal oxidation potentials for a number of ferrocenes showed that alkylferrocenes were more easily oxidized than ferrocene, while the opposite was true for the bridged compounds, possibly due to screening or to interaction of the middle C-atom with electron shells of the Fe atom. Thus, XXII with  $\text{CH}_2\text{N}_2$  in  $\text{Et}_2\text{O}$  gave 81 percent XLI,  $b_{0.05}$  100-10°. Treatment of the ferrocene derivative with  $\text{POCl}_3$  and  $\text{PhMeNCHO}$  gave the formyl compound [ferrocene derivative, purification, aldehyde, melting point (recrystallization solvent), percent yield, and melting point (recrystallization solvent) semicarbazone given]: XLI,  $\text{Al}_2\text{O}_3$  and distillation ( $b_{0.1}$  150-60°), 1, 1'-diethyl-3 (?)-( $\beta$ -carbomethoxyethyl)-3' (?) -formylferrocene (XLIII), —, 69, 87-91° ( $\text{Et}_2\text{O}$ -petr. ether); I (possibly containing a small amount 1, 2-isomer),  $\text{Al}_2\text{O}_3$  and crystallization, 1, 1': 3, 3'-bis (trimethylene) formylferrocene (XLIV), 88-9° (petr. ether), 81, —; XXXVIII,  $\text{Al}_2\text{O}_3$ -thin layer chromatography-recrystallization, 1, 1': 2, 2': 4, 4'-tris (trimethylene) formylferrocene (XLV), 109-13° (petr. ether), 52, 192-4° ( $\text{C}_6\text{H}_6$ -petr. ether). The aldehyde with  $\text{CH}_2(\text{CO}_2\text{H})_2$  gave the carboxyvinyl compound, usually containing some unsaturated malonic acid (aldehyde, products, percent yield, melting point,  $R_f$  value, and  $R_f$  value of the unsaturated malonic acid given): XLIII, 1, 1'-diethyl-3 (?)-( $\beta$ -carboxyethyl)-3' (?)-( $\beta$ -carboxyvinyl) ferrocene (XLVI), 85, —, 0.53, 0.18; XLIV, 1, 1': 3, 3'-bis (trimethylene)( $\beta$ -carboxyvinyl) ferrocene, 96, 147-50° (decomposition), 0.75, —; XLV, 1, 1': 2, 2': 4, 4'-tris (trimethylene) ( $\beta$ -carboxyvinyl) ferrocene (XLVIII), 91, 150-60° (decomposition), 0.74, 0.46. Heating the unsaturated malonic acid from XLV in refluxing xylene gave XLVIII. Hydrogenation of the carboxyvinyl compounds gave the carboxyethyl compounds (carboxyvinyl compound, catalyst, solvent, carboxyethyl compound, percent yield, melting point, and  $R_f$  value given): XLVI, 10 percent Pd-C,  $\text{EtOH}$ , 1, 1'-diethyl-3, 3' (?) -bis ( $\beta$ -carboxyethyl) ferrocene (XLIX), —, ( $b_{0.1}$  200-20°), 0.55; XLVII,  $\text{PtO}_2$ ,  $\text{AcOH}$ , 1, 1': 3, 3'-bis (trimethylene) ( $\beta$ -carboxyethyl) ferrocene (L), 83, 85-90°, 0.76; XLVIII,  $\text{PtO}_2$ ,  $\text{AcOH}$ , 1, 1': 2, 2': 4, 4'-tris (trimethylene) ( $\beta$ -carboxyethyl) ferrocene (LI), 85, 160° (decomposition), 0.74. XLIX contained some of the malonic



1.5460] and increasing  $R_f$  values (VII, 0.59; XLII, 0.78). XLII showed no nuclear magnetic resonance signal for a ring H. The formylation of XLI was assumed to occur heteroannularly for steric reasons. Oxidation potentials on the following compounds were determined (Mason and Rosenblum, CA 55, 2312f) at 20° in 2:32:15 Me<sub>2</sub>CO-AcOH-H<sub>2</sub>O by titration with 0.015N K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in 3:1 AcOH-H<sub>2</sub>O: ferrocene (270 mv.), VII, tetraethylferrocene, hexaethylferrocene, octaethylferrocene, XLII (-50 mv.), II (270? mv.), 1, 1'-bis (α-hydroxybenzyl) ferrocene (360 mv.), hydroxymethylferrocene (335 mv.), α-naphthylferrocene, α-thenylferrocene, diferrocenylmethane, benzylferrocene, and 1, 1'-dibenzylferrocene. The oxidation of II was in part irreversible and that of I completely irreversible.



131. Shanks, D. R.,  
Title not available, Inorg. Syn., Vol. 7, 1963, p. 201.

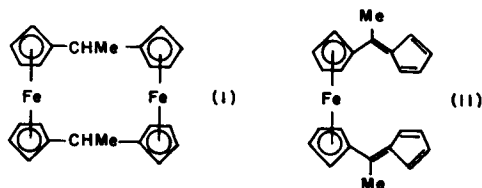
Refer to item No. 28 for abstract.

132. Sokolova, E. B., Shebanova, M. P., Chou, H.,  
SYNTHESIS OF FERROCENE ANALOGS, Zhurnal Obshchei Khimii, Vol. 33, 1963, pp. 217-220.

Refluxing alkylindenes with 1.5 moles BuLi in Et<sub>2</sub>O 2 hrs. gave 80-95 percent C<sub>4</sub>H<sub>10</sub>, while the solution of the Li derivative was treated with 0.6 mole FeCl<sub>2</sub> 1 hr. at room temperature and 2 hrs. at reflux and after treatment with aqueous HCl, gave the following ferrocene analogs after removal of starting material with superheated steam and sublimation of the residue in vacuo: bis (ethylindenyl) iron, violet-black; bis (allylindenyl) iron, violet-black; bis (butylindenyl) iron, 20 percent violet-black; bis (phenylindenyl) iron, 18 percent, black; bis (benzylindenyl) iron, 10 percent black, m. 131-3°. All were stable in dry air, but decomposed in hydrocarbons or ethers, yielding unidentified brown products. The following constants of starting materials were determined: 3-ethylindene, b<sub>745</sub> 224°, d<sub>20</sub> 0.9744, n<sub>D</sub><sup>20</sup> 1.5601; 3-butylindene, b<sub>17</sub> 129.5-30°, 0.9479, 1.5410; 3-allylindene, b<sub>5</sub> 191-2°, 0.9990, 1.5760; 3-phenylindene, b<sub>28</sub> 201°, 1.0826, 1.6345; 3-benzylindene, m. 33°, b<sub>7</sub> 166-7°.

133. Watts, W. E.,  
 THE [1.1] FERROCENOPHANE SYSTEM, American Chemical Society Journal, Vol. 88, No. 4, 1966, pp. 855-856.

1, 12-Dimethyl [1.1] ferrocenophane (I) was synthesized and characterized. I is obtained from the reduction of bis-fulvene (II) with  $\text{LiAlH}_4$  in tetrahydrofuran and subsequent treatment with  $\text{FeCl}_2$ . From the mixture of products I is separated chromatographically. I is crystallized from



ligroine in orange blades, m.  $182-4^\circ$ . The structure I is assigned on the basis of infrared P. M. R., and mass spectra.

#### B. Alkyl, Dialkyl, and Polyalkyl Ferrocenes

134. Cordes, J. F.,  
 FERROCENE AND ALKYLFERROCENES, German Patent 1,203,265 (Cl. C07f) 21 October 1965, Applied 10 April 1963, 10 pp., Addendum to German Patent 1,194,855 (see Fr. 1,341,880, CA 60, 6873a).

Ferrocene and its alkyl substituted derivatives were prepared by reducing  $\text{FeCl}_3$  in an organic solvent followed by treating with cyclopentadiene or an alkyl-substituted cyclopentadiene. The solvent used was an inert derivative of an organic carboxylic acid. Thus, into 120 g.  $\text{FeCl}_3$  in 300 ml. MeCN HCl was introduced for a short time and the mixture treated with a suspension of 20 g. Fe powder in 100 ml. MeCN. Within a few min., a solution of  $\text{FeCl}_3$  in MeCN formed and was treated with 800 ml. 30 percent tech. Na methyrate solution and treated at  $40-5^\circ$  with 132 g. monomeric cyclopentadiene. After 15-20 min., the mixture was added to 3:1 dilute  $\text{H}_2\text{SO}_4$  to dissolve all components except the ferrocene which was filtered off, and recrystallized to give 176 g. pure ferrocene.

135. Goldberg, S. I.,  
 PENTAETHANODIFERROCENE, American Chemical Society Journal, Vol. 84, 1962, p. 3022.

The product obtained by treatment of ferrocene with  $\text{AlCl}_3$  and  $(\text{ClCH}_2)_2$  (Nesmeyanov and Kochetkova, CA 53,

21856g) was produced when  $C_6H_6$  was used in place of  $(ClCH_2)_2$ . The structure proposed by Nesmeyanov and Kochetkova is rejected. The aliphatic C atoms in pentaethanoferrrocene come from a third ferrocene nucleus or its equivalent. The aliphatic C atoms probably exist as substituted cyclopentane rings (or a modified form).

136. Huffman, J. W., Keith, L. H., and Asbury, R. L.  
SOME REACTIONS OF CHLOROFERROCENE WITH  
ORGANOLITHIUM COMPOUNDS, Journal of Organic  
Chemistry, Vol. 30, 1965, p. 1600.

The reaction of chloroferrocene with butyllithium in hexane-tetrahydrofuran to afford butylferrocene, biferrocenyl, and some minor reaction products is reported. The same reaction when carried out in the presence of lithium piperidide affords also 1-ferrocenylpiperidine. The mechanism of these reactions is discussed.

137. Imperial Chemical Industries, Ltd., Macclesfield, England,  
FERROCENE DERIVATIVES, Fr Addendum 79,755, 25  
January 1963, British Applied 16 December 1959, 8 pp.,  
Addendum to Fr 1,305,312.

New ferrocene derivatives useful as hematinics are described: 1, 1'-bis (1-methyl-1-ethylpropyl) ferrocene; 1, 1'-bis (1, 1'-dimethylbutyl) ferrocene; 1, 1'-bis (1-methyl-1-ethylamyl) ferrocene; 1, 1'-bis (1-methylcyclohexyl) ferrocene. In an example, 250 parts (1-methyl-1-ethylpropyl) cyclopentadiene (I) is added to 38 parts of finely divided Na suspended in 500 parts tetrahydrofuran at 20-30°. The mixture is stirred a further hr. and cooled to 5-10°. Anhydrous  $FeCl_2$  (110 parts) is added during 1 hr., and the mixture stirred 24 hrs. at 20-5° and filtered. The filtrate is poured into  $H_2O$ , and the red oil formed is separated and washed with dilute aqueous  $HCl$ , and then with  $H_2O$ . On crystallization from  $EtOH$ , 1, 1'-bis (1-methyl-1-ethylpropyl) ferrocene is obtained, m. 34°. A solution containing 273 parts  $EtBr$  in 700 parts  $Et_2O$  is added to 59 parts  $Mg$  turnings and 250 parts  $Et_2O$  during 90 min. The mixture is stirred a further hr., after which 165 parts cyclopentadiene is added. Stirring is continued 24 hrs. at 20-30°, after which 300 parts 1-methyl-1-ethylpropyl chloride is added during 2 hrs. The mixture is stirred again for 24 hrs. at 20-30°, and then poured onto ice. The  $Et_2O$  layer is separated, washed with  $H_2O$  and dried



over  $\text{Na}_2\text{SO}_4$ , and distilled to give (1-methyl-1-ethylpropyl) cyclopentadiene,  $b_{0.4}$   $38^\circ$ .

138. King, R. B. and Bisnette, M. B.,  
 $\pi$ -CYCLOPENTADIENYL- $\pi$ -INDENYLIRON, Angewandte Chemie, Vol. 75, No. 13, 1963, p. 642.

Refer to item No. 112 for abstract.

139. Leigh, T.,  
FERROCENE DERIVATIVES, British Patent 898,633,  
14 June 1960, Applied 27 January 1960, 4 pp., Addendum to  
British Patent 819,108 (CA 54, 7732b).

The compounds described are useful as hematinics. The acylferrocene compounds are prepared by treating ferrocene with the appropriate acid halide in the presence of anhydrous HF. Thus, 48 parts of  $\alpha$ ,  $\alpha$ -diethylacetyl chloride were added slowly with stirring to 150 parts of anhydrous HF at  $0^\circ$ , followed by the addition of 45 parts of ferrocene during 15 min., the temperature raised to  $20^\circ$ , and after one hr. poured on ice, filtered, washed, dried, and crystallized to give ( $\alpha$ ,  $\alpha$ -diethylacetyl) ferrocene (I), m.  $94^\circ$  (petr. ether). The process was repeated, using 47 parts of the respective acyl halide to prepare: ( $\alpha$ -butyl- $\alpha$ -isopropylacetyl) ferrocene, m.  $-10^\circ$ ; ( $\alpha$ ,  $\alpha$ ,  $\alpha$ -triethylacetyl) ferrocene, a red oil,  $n_D^{24}$  1.5800. The acylferrocenes are reduced by the Clemmensen process to the corresponding alkylferrocenes. Thus, Zn-Hg, obtained from 20 parts of granulated Zn, was added to a mixture of 40 parts of EtOH, 60 parts of concentrated aqueous HCl, and six parts of I, the mixture stirred and refluxed for 6 hrs. and the precipitated oil decanted and fractionally distilled to give (2-ethylbutyl) ferrocene,  $b_{0.1}$   $104^\circ$ . Similarly obtained were: (2-isopropylhexyl) ferrocene,  $b_{0.1}$   $117^\circ$ ; (2, 2-diethylbutyl) ferrocene,  $b_{0.1}$   $103^\circ$ .

140. Leigh, T.,  
FERROCENE DERIVATIVES CONTAINING TERTIARY  
ALKYL GROUPS. SYNTHESIS BY THE FRIEDEL-CRAFTS  
AND OTHER METHODS, Chemical Society Journal, September  
1964, pp. 3294-3302.

Contrary to a previous report, the alkylation of ferrocene with tert-BuCl under Friedel-Crafts conditions proceeds

smoothly, and mono-, 1, 1'-di-, 1, 3-di-, 1, 1', 3-tri-, and 1, 1', 3, 3'-tetra-tert-butylferrocenes can be isolated crystalline. 1, 1'-Di-tert-alkylferrocenes are also prepared from the corresponding tert-alkylcyclopentadienes, which are obtained by treating cyclopentadienylmethyl halides with tert-alkyl halides. Alkylferrocenes containing tert-alkyl groups separated from the nucleus by 1 and 2 C atoms are described. From the reaction between pivaloyl chloride and ferrocene in the presence of  $\text{AlCl}_3$  are obtained various products, including 1, 1'-dipivaloyl-3, 3'-di-tert-butylferrocene. A synthesis of neopentylchloropentadiene via ethoxymethylcyclopentadiene is recorded.

141. Morehouse, E. L.,  
CYCLOPENTADIENYL-TYPE METALLIC COMPOUNDS,  
U. S. Patent 3,071,605 (Cl. 260-429), 1 January 1963,  
Applied 15 February 1955, 5 pp.

Refer to item No. 116 for abstract.

142. Nesmeyanov, A. N. and Kochetkova, N. S.,  
ALKYLATION OF FERROCENE, Doklady Akademii Nauk  
SSSR, Vol. 109, 1956, pp. 543-545.

Alkylation of ferrocene (I) by a Friedel-Crafts method, which supports the aromatic character of I, was accomplished by using excess alkyl halide as the solvent. To 40 g. I (m.  $173^\circ$ ) in 150 ml. EtBr was added 15 g.  $\text{AlCl}_3$  and the mixture refluxed 5 hrs., treated with ice, then with ice 10 percent HCl, the two-layer mixture treated with 10 g.  $\text{Na}_2\text{SO}_3$ , filtered and the lower red layer separated, dried, freed of EtBr and the residue heated in vacuo subliming 1.5 g. I; the residue was fractionated yielding 4 percent Et-I,  $b_5$   $107-8^\circ$ ,  $n_D^{20}$  1.6011,  $d_{20}$  1.2470, 3.5 percent di-Et-I,  $b_5$   $120-3^\circ$ ,  $n_D^{20}$  1.5852, and 3.5 percent mixed tri-Et-I isomers,  $b_5$   $145-53^\circ$ . Similarly BuCl gave 7.6 percent Bu-I,  $b_{3.5}$   $108^\circ$ ,  $n_D^{20}$  1.5701,  $d_{20}$  1.1859, 5.2 percent di-Bu-I,  $b_{3.5}$   $155-7^\circ$ ,  $n_D^{20}$  1.5649,  $d_{20}$  1.1432, and 16.5 percent mixed penta-Bu-I isomers,  $b_7 \times 10^{-4}$   $145-6^\circ$  (analytical sample),  $b_7 \times 10^{-4}$   $138-50^\circ$ , f. p.  $-19^\circ$ .  $\text{PhCH}_2\text{Cl}$  gave from 20 g. I, some 15 g. unreacted I and 1.5 g. benzyl-I, m.  $55-7^\circ$ . Reaction of 20 g. I, 75 ml.  $(\text{CH}_2\text{Cl})_2$ , and 6 g.  $\text{AlCl}_3$ , 7 g. unreacted I removed by steam distillation with superheated steam, and a tarry residue taken up in 1:1  $\text{HNO}_3$  then treated

with  $\text{Na}_2\text{SO}_3$ , gave yellow diferrocenylethane, 27 percent m.  $135^\circ$  (sealed tube). Higher proportions of  $\text{AlCl}_3$  and longer reaction times gave a brownish high polymer which contained Fe and showed ion-exchange properties as a reduction-oxidation resin, oxidizable with dichromate and reducible with ascorbic acid.

143. Nesmeyanov, A. N., Kochetkova, N. S., Vitt, S. V., Bondarev, V. B., and Kovshov, E. I.,  
ALKYLATION OF FERROCENE, Doklady Akademii Nauk SSSR, Vol. 156, No. 1, 1964, pp. 99-101.

Ferrocene treated in dry heptane with 1 mole  $\text{LiAlH}_4$  followed by varying amounts of  $\text{AlCl}_3$  and  $\text{EtBr}$ , added over 1.5 hrs. at  $60^\circ$ , gave mono-, di-, and triethylferrocenes, separated by gas chromatography in a Ag capillary column with Apiezon L as the stationary phase. The analyses were possible to within 3 percent and the reaction gave up to 50 percent mono- and diethyl derivatives. Similar alkylation with  $\text{tert-BuCl}$  gave mono-, di-, tri (m.  $85^\circ$ ), and tetra- $\text{tert-butylferrocenes}$  (m.  $195-6^\circ$ ). The nuclear magnetic resonance spectra of these showed no isomerization of the  $\text{tert-Bu}$  group.

144. Paushkin, Y. M., Vishnyakova, T. P., Sokolinskaya, T. A., Zimina, K. I., and Kotova, G. G.,  
ALKYLATION OF FERROCENE BY OLEFINS IN THE PRESENCE OF  $\text{BF}_3$  AND  $\text{AlCl}_3$ , Neftekhimiya, Vol. 3, No. 2, 1963, pp. 280-284.

Alkylations of ferrocene (I) by olefins were carried out in n-heptane 5 hrs. at  $20-140^\circ$  in an autoclave. The molar ratio of I to olefins was 1:1-1.3; the amount of catalyst was 25 percent of the weight of the reaction mixture. The alkylation mixture was purified by fractional distillation at 3-4 mm. The following iso-olefins were used:  $\text{C}_4\text{H}_8$  (II),  $\text{C}_5\text{H}_{10}$  (III),  $\text{C}_8\text{H}_{16}$  (IV), and  $\text{C}_{12}\text{H}_{24}$ . The yield of dialkyl- and polyalkylferrocenes decreased with the increasing molecular weight of olefins used. The yield of polysubstituted ferrocenes was increased by use of higher reaction temperature. The most effective catalyst was  $\text{H}_3\text{PO}_4 \cdot \text{BF}_3$ , which mostly afforded mono- and dialkyl derivatives (according to infrared spectra substituted on one ring). The yields of mono- and

dialkylferrocenes after alkylation by II were 45 and 26 percent; by III, 25 and 20 percent; by IV, 50 and 4 percent. Many polyalkyl derivatives were obtained when  $\text{AlCl}_3$  was used.  $\text{BF}_3$  etherate also catalyzed alkylations of I (in contrast to  $\text{C}_6\text{H}_6$ , where polymerization occurred). Alkylferrocenes were prepared (alkyl given):  $\text{C}_8\text{H}_{17}$ ,  $b_3$  155-60°,  $n_D^{20}$  1.5626,  $d_{20}$  1.1205; and  $(\text{C}_8\text{H}_{17})_2$ ,  $b_3$  230-5°,  $n_D^{20}$  1.5558,  $d_{20}$  1.0824.

145. Pisareva, S. A., Sokolova, E. B., and Shebanova, M. P.,  
SYNTHESIS OF FERROCENE HOMOLOGS, Tr. Mosk.  
Khim. -Tekhnol. Inst., No. 46, 1964, pp. 18-22 (In Russian).

Diheteroannular substituted homologs of ferrocene, 1, 1'-di (sec-butyl) cyclopentadienyliron, 1, 1'-di (3-pentyl) cyclopentadienyliron, and 1, 1'-bis ( $\alpha$ -phenylethyl) cyclopentadienyliron (Ia-c), were synthesized by the action of  $\text{FeCl}_2$  on adducts of methylethylphenylfulvene (II), diethylphenylfulvene (III), and methylphenylfulvene (IV) with  $\text{LiAlH}_4$ . II, III, and IV were obtained by condensation of cyclopentadiene (V) with  $\text{EtMeCO}$ ,  $\text{Et}_2\text{CO}$ , and  $\text{BzMe}$ . One mole ketone was added to 1 mole V (obtained by depolymerization of dicyclopentadiene) while cooling; then 20 ml. of a 20 percent KOH solution in MeOH was added and after 12 hrs. the mixture was steam distilled. Given are compound, percent yield, boiling point/mm., and  $n_D^{20}$ : II, 20.0, 65-67°/17, 1.5350; III, 16.2, 75°/13, 1.5300; IV, 23.8, 128°/10, 1.5590.  $\text{LiAlH}_4$  (0.45 mole) ground in a N atm. was added to 200 ml. ether, the mixture cooled to 20°, after 15 min. 0.19 mole II, III, or IV in 200 ml. ether added, the mixture cooled to 20°, 0.21 mole  $\text{FeCl}_2$  in 60 ml. tetrahydrofuran added over a period of 30 min., the mixture stirred several hrs. in a N atm., and after 12 hrs. decomposed with MeOH to yield Ia-c. Given are I, percent yield, boiling point/mm., melting point,  $n_D^{20}$  and  $d_{20}$ : a, 22.9, 184°/17, -50°, 1.5530, 1.1015; b, 23.2, 192°/15, 3.0°, 1.5550, 1.1028; c, 25.5, 235°/5, -12°, 1.6050, 1.1621. From Referativny: Zhurnal Khimii, 1965, Abstract No. 5Zh334.

146. Rausch, M. D., Vogel, M., and Rosenberg, H.,  
DERIVATIVES OF FERROCENE. PART III. THE PREPARA-  
TION OF SOME ACYLFERROCENES AND ALKYLFERRO-  
CENES, Charles J. Cleary Awards for Papers on Material  
Sciences, Washington, D. C., Library of Congress, Science  
and Technology Division, 1962, pp. 121-124 (N63-13243).

Several new acylferrocenes and 1, 1'-diacylferrocenes  
have been prepared and reduced to the corresponding alkyl-  
ferrocenes and 1, 1'-dialkylferrocenes. Attempts to directly  
alkylate ferrocene resulted in mixtures of polyalkylated  
products.

147. Riemschneider, R.,  
FERROCENE AND RELATED COMPOUNDS VII. BIS  
(ISODICYCLOPENTADIENYL) IRON, Zeitschrift fuer  
Naturforschung, Vol. 17b, No. 2, 1962, p. 133 (cf. Ann.,  
Vol. 646, 1961, p. 10, CA 55, 25898h).

To EtMgBr from 11 g. EtBr, 2.4 g. Mg, and 50 ml.  
Et<sub>2</sub>O was added 50 ml. dry xylene and the Et<sub>2</sub>O distilled.  
Under N, 10 g. isodicyclopentadiene (I) in 50 ml. xylene was  
added dropwise. The mixture was refluxed 2 hrs., cooled,  
ether added, and then a solution of 12 g. iron (II) acetonylace-  
tate-2C<sub>5</sub>H<sub>5</sub>N in 100 ml. xylene at 15°. After stirring, the  
mixture was kept at room temperature for 2 days under N  
and then warmed for 1 hr. at 55-60°. The brownish solution  
was poured onto a mixture of ice and aqueous NH<sub>4</sub>Cl, the  
xylene solution separated, washed, and dried. After removal  
of solvent and distillation of unconverted I, the residue was  
taken up with acetone, filtered through C, and chilled to give  
yellow-brown crystals, m. 150-70°. Recrystallization from  
acetone or HCONMe<sub>2</sub> gave pure bis (isodicyclopentadienyl)  
iron (II), m. 172.5-3°, in 20 percent yield.



148. Royal College of Science and Technology, Glasgow, Great Britian,

PREPARATION OF NOVEL ORGANOMETALLIC COMPOUNDS OF THE TRANSITION ELEMENTS, THIRD QUARTERLY TECHNICAL STATUS REPORT, 1 MARCH-31 MAY 1964 by P. L. Pauson, 1964, AD-449 203, N64-32453, Contract No. DA-91-591-EUC-3101.

The first use of a pyrrole bearing a functional substituent in the synthesis of a manganese complex (I: R = Me) was reported previously. This has been extended to the lower homolog 3-acetyl-2-methylpyrrole, which affords the analogous complex (I: R = H); both these pyrroles have been used in the preparation of appropriately substituted azaferrocenes. Reinvestigation of the reaction of indolylpotassium with iododicarbonylcyclopentadienyliron not only confirmed the formation of dicarbonyl  $\sigma$ -indolylcyclopentadienyliron, but led also to the isolation of the expected  $\pi$ -indolylcyclopentadienyliron, as an unstable oil identified spectroscopically. The structure of the dicarbonyldiallyliron described in the preceding report has now been confirmed by its synthesis from allylmagnesium chloride and iodotricarbonylallyliron.

149. Schlogel, K., Mohar, A., and Peterlik, M.,  
PREPARATION OF ALKYLFERROCENES FROM ACYLFERROCENES BY REDUCTION WITH LITHIUM-ALUMINUM HYDRIDE-ALUMINUM CHLORIDE, (Foreign title not available), Translated into English from the German by U. S. Army Missile Command, Redstone Arsenal, Alabama, RSIC-536 (Montashefte fuer Chemie, Vol. 92, No. 4, 1961, pp. 921-926).

Alkylferrocenes can be prepared easily by reducing the corresponding acylferrocenes with  $\text{LiAlH}_4\text{-AlCl}_3$ . In all cases investigated, which comprised seven mono- and five diacylferrocenes ranging from ferrocenealdehyde to 1, 1'-dibenzoylferrocene (Table 1), the yields of the alkyl (aralkyl) - ferrocenes obtained were practically theoretical. The products were characterized by their  $R_f$  values and, when they were oily, also by their refraction indices (Table 1). It could be shown that under the conditions applied ferrocenyl carbinols and ferrocenyl ethers containing the group  $\text{Fc}-\text{C}-\text{O}-$  were also reduced to (aralkyl) ferrocenes.

150. Sokolova, E. B., Shebanova, M. P., Chou, H., and Pisareva, S. A.,

UTILIZATION OF FULVENES FOR THE SYNTHESIS OF HOMOLOGS AND ANALOGS OF FERROCENE, Zhurnal Obshchei Khimii, Vol. 34, No. 8, 1964, pp. 2693-2696.

3-Substituted indenenes treated with  $\text{PhCH:CHCHO}$  according to Thiele (Ber. 33, 3399 (1900)) gave 3-substituted 8-styrylbenzofulvenes (percent yield, 3-substituent, and melting point given): 47, Ph, 129.5-30.5°; 30,  $\text{PhCH}_2$ , 161-2°; 15,  $\text{CH}_2\text{:CHCH}_2$ , 110°; 11.2, Et, 109-10°. A solution of 0.45 mole  $\text{LiAlH}_4$  in  $\text{Et}_2\text{O}$  treated with 0.19 mole appropriate fulvene (exothermic), followed by 0.21 mole  $\text{FeCl}_2$  in tetrahydrofuran gave in 1 day under N atm.



the following I: (R, percent yield, boiling point, melting point,  $n_D^{20}$ , and  $d_{20}$  given):  $\text{MeEtCH}$ , 22.9,  $b_{17}$  184°, -50°, 1.5530, 1.1015;  $\text{Et}_2\text{CH}$ , 23.2,  $b_{15}$  192°, 3°, 1.5550, 1.1028;  $\text{MeCHPh}$ , 25.5,  $b_5$  235°, -12°, 1.6050, 1.1621. The reaction of 3-phenyl-8-styrylbenzofulvene gave a black undistillable product, containing 8.34 percent Fe. The reaction of the 3-benzyl analog gave unstable products which could not be preserved.

151. Vishnyakova, T. P., Paushkin, Y. M., and Sokolinskaya, T. A.,

ALKYLATION OF FERROCENE WITH DI- AND TRIISOBUTYLENE AND CYCLOHEXENE, Zhurnal Obshchei Khimii, Vol. 33, No. 11, 1963, pp. 3685-3687.

Ferrocene and di- or triisobutylene were found to undergo the alkylation reaction in the presence of 25 percent (by weight)  $\text{BF}_3 \cdot \text{H}_3\text{PO}_4$ . With equimolar amounts of the reactants, with diisobutylene, up to 92.5 percent monoalkylferrocene, with 16-21 percent dialkylated product was formed at 20°; elevation of the temperature to 60 and 100° increased the yield of the dialkylated product to up to 21 percent (similar effect was produced by excess olefin in the mixture). Excess

olefin also resulted in formation of polyalkylates. Triisobutylene reacted best at 140° and gave 37.5 percent mono- and 50 percent dialkylated product, with 12.5 percent polyalkylates. Cyclohexene reacted well at 60° and with 50-100 percent excess olefin gave 51-74 percent mono-, 26-36 percent di-, and 0-12.5 percent polyalkylated products. With eight-fold excess cyclohexene these yields were 18.2 percent, 67.7 percent, and 14.1 percent. Monoisooctylferrocene (I)  $b_3$  155-60°,  $n_D^{20}$  1.5626,  $d_{20}$  1.1205; diisocrylferrocene  $b_3$  230-5°, 1.5558, 1.0824; monoisododecylferrocene  $b_3$  190-5°, 1.5561, -; cyclohexylferrocene,  $b_5$  157-62°, 1.5989, 1.2220; dicyclohexylferrocene  $b_5$  208-15°, 1.5924, 1.1965. (The term isooctyl and isododecyl is provisionally used by the authors.) The infrared spectrum of I is shown.

### C. Acyl Ferrocenes

152. Asbury, R. L., Jr.,  
THE ACID-CATALYZED REACTIONS OF SELECTED  
 $\beta$ -FERROCENYLPROPIONIC ACIDS, University Microfilms  
(Ann Arbor, Michigan) Order No. 65-9529.

A new series of substituted  $\beta$ -ferrocenylpropionic acids has been prepared, and the mode of reaction of each member under conditions normally employed for intramolecular acylation has been studied experimentally.

For each case studied, the formation of a particular product (or the alternative failure of its formation) is rationalized in terms of qualitative thermodynamic considerations.

Of particular interest is the preparation of 1, 2-( $\alpha$ -keto- $\beta$ ,  $\beta$ -dimethyltrimethylene) ferrocene, "ferrocenocyclopentadienone," and "1, 2-( $\alpha$ -ketotrimethylene) ferrocene," the former being the first authentic example of a ferrocene derivative possessing only the unique homoannular disposition of a three-carbon cycle.

153. Bieber, T. I., and Dorsett, M. T.,  
SYNTHESIS OF  $\alpha$ -(FERROCENYLMETHYL) KETONES BY  
THE ENAMINE METHOD, Journal of Organic Chemistry,  
Vol. 29, No. 7, 1964, pp. 2028-2030.

By analogy with benzyl halides, ferrocenylmethyl halides should effect predominant C-alkylation of enamines.

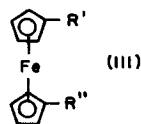
(Ferrocenylmethyl) trimethylammonium iodide (I) was used successfully in the alkylation of the pyrrolidine enamines of



cyclopentanone and cyclohexanone, respectively. N-cyclohexenylpyrrolidine and I in anhydrous MeCN refluxed (N atm.) 24 hrs. with evolution of NMe<sub>3</sub> and the red-brown mixture refluxed 3 hrs. in H<sub>2</sub>O and 6N HCl yielded 88 percent 2-(ferrocenylmethyl) cyclohexanone (II). The same reaction in moist MeCN gave a reduced yield of II and N-(ferrocenylmethyl) pyrrolidine (III). Similar alkylation of N-cyclopentenylpyrrolidine with I yielded 54 percent oily 2-(ferrocenylmethyl) cyclopentanone (IV). Use of moist MeCN similarly gave some III. The ultraviolet spectra of II and IV gave no evidence for intermolecular interaction between Fe and the CO group in the respective side chains.

154. Dabard, R., and Gautheron, B.,  
ACTION OF FERROCENE ON CHLORIDES AND ANHYDRIDES,  
Comptes Rendus, Vol. 254, 1962, pp. 2014-2016.

AlCl<sub>3</sub> and phenylacetyl chloride (I) in CH<sub>2</sub>Cl<sub>2</sub> added dropwise to ferrocene (II) give after hydrolysis and extracting 80 percent phenylacetylferrocene (III, R' = COCH<sub>2</sub>Ph, R'' = H), m. 130°; oxime m. 150°. If II is poured into I and AlCl<sub>3</sub>, III (R' = R'' = COCH<sub>2</sub>Ph), m. 148°, 60 percent (dioxime, m. 202-4°) is obtained. Reduction of the ketones yields the corresponding alcohols: III (R' = CH (OH) CH<sub>2</sub>Ph, R'' = H), m. 64°, and III (R' = R'' = CH (OH) CH<sub>2</sub>Ph), m. 140°. Clemmensen reduction yields, respectively, III (R' = CH<sub>2</sub>CH<sub>2</sub>Ph, R'' = H), m. 59°, and III (R' = R'' = CH<sub>2</sub>CH<sub>2</sub>Ph), m. 70°. The following III were similarly prepared from toluylyl, thenoyl, and pyrrolecarbonyl chlorides (R' and R'' given): p-MeC<sub>6</sub>H<sub>4</sub>CO, H, b. 135°; m-MeC<sub>6</sub>H<sub>4</sub>CO, H, b. 220°; p-MeC<sub>6</sub>H<sub>4</sub>CO, H, m. 132°; 2-thenoyl, H, m. 125°; 2-furoyl, H, m. 80°; 2-pyrrolyl, H, m. 163°. Bromosuccinic anhydride and phthalic anhydride give III (R' = COCH:CHCO<sub>2</sub>H, R'' = H), m. 178°, and III (R' = o-HO<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>CO, R'' = H), m. 198°, 33 percent, respectively. cis-Hexahydrophthalic anhydride yields cis-2-ferrocenylcarbonylcyclohexanecarboxylic acid, m. 176°, which is reduced to 2-ferrocenylmethylcyclohexanecarboxylic acid, m. 120°. Me vinyl ketone and Me acrylate do not react.



155. Decombe, J., Dormond, A., and Ravoux, J. P.,  
SEVERAL NEW DERIVATIVES OF FERROCENE, Comptes  
Rendus, Vol. 259, No. 23, 1964, pp. 4289-4291 (In French).

Refer to item No. 103 for abstract.

156. Decombe, J., Ravoux, J. P., and Dormond, A.,  
SOME NEW DERIVATIVES OF FERROCENE, Comptes  
Rendus, Vol. 258, No. 8, 1964, pp. 2348-2349.

Fe = ferrocenyl. Condensation of dimethylaminomethylferrocene methiodide (Ia) with  $\text{AcCHNaCO}_2\text{Et}$  in refluxing EtOH gave 85 percent red  $\text{FCCH}_2\text{CHAcCO}_2\text{Et}$  (I), b. 168-70°. I, shaken with excess  $\text{NaHCO}_3$  for 15 hrs. and then acidified gave 72 percent  $\text{FeCH}_2\text{CH}_2\text{COMe}$  (II), m. 45-6° (oxime m. 142°), and 16 percent  $\text{FeCH}_2\text{CH}_2\text{CO}_2\text{H}$ . Hydrogenation of II with Na in EtOH gave 96 percent  $\text{FeCH}_2\text{CH}_2\text{CHMeOH}$ , b<sub>1</sub> 149-52°; p-nitrobenzoate m. 80-1°. The reaction of Ia with  $\text{NCCHNaCO}_2\text{Et}$  (III) in refluxing EtOH was very slow and even after 100 hrs. only 60 percent of the expected evolution of  $\text{Me}_3\text{N}$  had occurred. The isolated product was an uncharacterized oil. The reaction was rapid, however, when III was prepared from a Na sand in MePh. The reaction was complete in 90 min. in refluxing MePh and gave 40 percent  $\text{Fe}_2\text{C}(\text{CN})\text{CO}_2\text{Et}$  (IV), m. 132°. IV was converted into an amide, m. 232° (decomposed partly 190-5°), by the action of KOEt in refluxing EtOH.

157. Directorate of Materials and Processes, Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio,  
CONFERENCE ON HIGH TEMPERATURE POLYMER AND FLUID RESEARCH, A STUDY OF THE FRIEDEL-CRAFTS ACYLATION OF FERROCENE WITH PERFLUOROCARBOXYLIC ACID DERIVATIVES by S. G. Cottis and H. Rosenberg, August 1962, X63-15750, X63-15709 22-07, pp. 637-649 (Unclassified Report).

Investigation of synthetic approaches to the perfluoroalkylferrocenyl ketones.  $\text{C}_5\text{H}_5\text{FeC}_5\text{H}_4\text{COR}_f$ , is discussed. Acylation of ferrocene with perfluorocarboxylic acid anhydrides was carried out to yield the desired perfluoroacylferrocenes. The reactions were conducted in methylene chloride using anhydrous aluminum chloride as the catalyst. In these acylations, only monosubstituted ketones were isolated (30-40 percent yield) even when conditions favoring diacylation

were employed. The yield of perfluoropropylferrocenyl ketone from the reaction of perfluorobutyl chloride and ferrocene was found to be less than 10 percent. When benzene, ferrocene, and anhydrous hydrogen fluoride were reacted together, a phenylcyclopentylferrocene was obtained. This indicated that phenylcyclopentylferrocene is not formed through a cyclopentenyl intermediate.

158. Dormond, A., Ravoux, J. P., and Decombe, J.,  
CHEMISTRY OF FERROCENE, Compt. Rend. Ser. C.,  
Vol. 262, No. 11, 1966, pp. 940-942 (in French).

The Na derivative of  $\alpha$ -ferrocylacetylacetone (CA 62, 11852b) and  $\text{BrCH}_2\text{CO}_2\text{Et}$  (I) gives 59 percent brown-orange Et  $\beta$ ,  $\beta$ -diacetylferrocenylbutyrate, m.  $87^\circ$  (petroleum ether), sapond. in 80 percent yield to dark brown  $\beta$ -acetylferrocenylbutyric acid (II), m.  $149-50^\circ$  ( $\text{Et}_2\text{O}$ -petroleum ether). II in  $\text{CH}_2\text{Cl}_2$  is cyclized by  $(\text{F}_3\text{CCO})_2\text{O}$  (III) to give 23 percent yellow 2, 3-ferroceno-5-acetyl-2-cyclohexen-1-one, m.  $59^\circ$  ( $\text{Et}_2\text{O}$ -petroleum ether). Et ferrocylmalonate (Hauser and Lindsay, CA 52, 5393b), converted to the Na derivative (IV), reacts with I to give a red oil, mainly the Et ester of  $\alpha$ -carboxy- $\alpha$ -ferrocylsuccinic acid, sapond. by alcoholic  $\text{K}_2\text{CO}_3$  to the acid, m.  $247^\circ$  (decomposition). Similarly, IV and  $\text{PhCH}_2\text{Cl}$  gives the oily Et ferrocylbenzylmalonate and the corresponding acid (V), m.  $221^\circ$  (decomposition). V decarboxylates at  $200^\circ$  to 90 percent orange ferrocylbenzylacetic acid (VI), m.  $138^\circ$ . III cyclizes VI in  $\text{CH}_2\text{Cl}_2$  to 79 percent red-orange 1, 1'-( $\alpha$ -oxo- $\beta$ -benzyltriethylene)-ferrocene (VII), m.  $141^\circ$  (hexane), also prepared in very low yield from V and III. Et diferrocylmalonate (VIII), m.  $138^\circ$ , is prepared in 74.5 percent yield by treating equimolar amounts of IV and dimethylaminomethylferrocene methiodide in  $\text{HCONMe}_2$ . Sapon. of VIII forms 84 percent diferrocylmalonic acid dihydrate, converted at  $110^\circ$  to the anhydrous acid (IX), m.  $234^\circ$ . Decarboxylating IX at  $165^\circ$  yields 88 percent diferrocylacetic acid, m.  $164^\circ$ , cyclized by III to 1, 1'-( $\alpha$ -oxo- $\beta$ -ferrocyltriethylene) ferrocene (X), m.  $218^\circ$  ( $\text{Et}_2\text{O}$ ), in 80 percent yield. Boiling III and IX in  $\text{CH}_2\text{Cl}_2$  produces much tar, 30 percent X, and 12 percent red  $\beta$ ,  $\beta$ -bis-[1, 1'-( $\alpha$ -oxo-triethylene) ferrocene] spiran, m.  $291^\circ$ .

159. Dormond, A., Ravoux, J. P., and Decombe, J.,  
NEW FERROCENE DERIVATIVES, Société Chimique de  
France, Bulletin, No. 3, 1966, pp. 1152-1153 (In French).

Ferrocene-ketone compounds  $\text{FcCOR}$  ( $\text{Fc}$  = ferrocene) were converted to tertiary alcohols  $\text{FcCR}(\text{OH})\text{CH}_2\text{CO}_2\text{Et}$  (I) by the Reformatsky reaction. I was treated with  $\text{P}_2\text{O}_5$  in benzene to give ethylenic esters  $\text{FcCR}:\text{CHCO}_2\text{Et}$ , which was saponified. The following compounds are reported: 3-ferrocenylcrotonic acid, m.  $202^\circ$ ; 2-ferrocenyl-1-butene-1, 4-dicarboxylic acid, m.  $182^\circ$ ; 3-ferrocenyl-o-carboxycinnamic acid, m.  $242^\circ$ ; ferrocenyl-1, 1'-trimethylene- $\alpha$ -ethylidenoic acid (sec), m.  $239^\circ$ ; ferrocene-2, 3-cyclohexene-2-ethylidenoic acid (sic), m.  $143-5^\circ$ , and the saturated hydrogenation products of all except the last named.

160. Egger, H., and Schlogel, K.,  
FERROCENE DERIVATIVES. XXII. ON THE FORMATION OF  
1, 3-DIFERROCENYLPROPENONE FROM FERROCENYL-  
CHLOROMETHYLCARBINOL, Journal of Organometallic  
Chemistry, Vol. 2, No. 5, 1964, pp. 398-409 (In German),  
(cf. CA 61, 14078h).

Treatment of ferrocenylchloromethylcarbinol (I) with  $\text{EtO}^-$  in the presence of O gives in a fast reaction up to 50 percent of 1, 3-diferrocenylpropenone (II). In a first step via the (not isolable) ferrocenyl epoxide by fast isomerization, ferrocenylacetaldehyde (III) is formed. This important intermediate could be synthesized by an independent route. With  $\text{EtO}^-$  and O or with  $\text{ArCHO}$ , III furnishes the same products as I. After aldol condensation of III and subsequent oxidation to a hydroperoxide the latter is cleaved into II and  $\text{HCO}_2\text{H}$ , which could be detected (as ester) by gas chromatography. Ferrocenylpropenals are described, which are obtained, e. g., by condensation of III with benz- or 2-thiophenealdehyde; they could be isolated as geometrical isomers and were of importance with regard to the elucidation of the reaction sequence  $\text{I} \rightarrow \text{III}$ . The ultraviolet absorption maximum of several unsaturated ferrocenyl ketones and aldehydes are reported.

161. Falk, H. and Schlogel, K.,  
FERROCENE DERIVATIVES. XXIV. FERROCENE  
ASYMMETRY. 3. CONFIGURATION OF MONO- AND BIS  
( $\alpha$ -OXOTETRAMETHYLENE) FERROCENE, Monatshefte  
für Chemie, Vol. 96, No. 1, 1965, pp. 266-275 (In German)  
(cf. CA 62, 10459b).

The absolute configuration of (+)-1, 2- ( $\alpha$ -oxotetramethylene) ferrocene [ferroceno [1, 2] cyclohexanone] (I) was established as (R) by conversion to the exocarbinol (II), which was resolved by the  $\alpha$ -phenylbutyric anhydride method (Horeau, CA 58, 11194e). The configurations of the isomeric (cis- and trans-) bis ( $\alpha$ -oxotetramethylene) ferrocenes (III and IV, respectively) were attributed as follows: the lower melting bis (ketone) (m.  $160^{\circ}$ ) is the racemate (trans) and the higher melting (m.  $170^{\circ}$ ) is the meso (cis) form; the dextrorotatory ketone probably has the (R), (R<sup>1</sup>) configuration. I (0.8 g.),  $[\alpha]_D^{20} 510^{\circ}$  (EtOH) in 5 ml. absolute tetrahydrofuran (THF) was added to 0.1 g. LiAlH<sub>4</sub> in 3 ml. absolute THF, the mixture stirred 30 min., decomposed with moist Et<sub>2</sub>O, filtered, and evaporated to give 0.75 g. ferroceno [1.2] cyclohex-1-en-3-ol (II) (exo-endo 1:10). This in 2 ml. absolute C<sub>6</sub>H<sub>6</sub> was acetylated with 1.0 g. Ac<sub>2</sub>O, 1 ml. absolute C<sub>6</sub>H<sub>6</sub>, and 3 ml. C<sub>5</sub>H<sub>5</sub>N 16 hrs. at room temperature, and the acetate mixture diluted with H<sub>2</sub>O and C<sub>6</sub>H<sub>6</sub>, washed with N HCl, NaHCO<sub>3</sub>, and H<sub>2</sub>O, dried, and evaporated in vacuo to give 0.85 g. mixture of acetates. The mixture of epimeric acetates was refluxed 48 hrs. in 250 ml. 80 percent aqueous Me<sub>2</sub>CO and this solution then diluted with H<sub>2</sub>O, concentrated in vacuo, and extracted with Et<sub>2</sub>O, which was evaporated to give 0.6 g. exo-II, which was chromatographed on alumina to give 0.55 g. exo-II,  $[\alpha]_D^{20} 113 \pm 5^{\circ}$  (c 1.2, EtOH). exo-II (0.55 g.) in 10 ml. absolute C<sub>5</sub>H<sub>5</sub>N was treated with 2.5 g. (EtCHPhCO)<sub>2</sub>O 15 hrs. at room temperature and the mixture diluted with H<sub>2</sub>O and C<sub>6</sub>H<sub>6</sub>, and shaken with 0.2N Na<sub>2</sub>CO<sub>3</sub>. After washing with C<sub>6</sub>H<sub>6</sub>, the combined aqueous extracts were acidified with concentrated HCl and extracted with C<sub>6</sub>H<sub>6</sub>, which was evaporated to give EtCHPhCO<sub>2</sub>H,  $[\alpha]_D^{18} 0.79^{\circ}$ . The C<sub>6</sub>H<sub>6</sub> fraction from the original separation was washed with N HCl, 5 percent HOCH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>, and H<sub>2</sub>O, dried, and evaporated to give, after preparative chromatography, eluting with 15:1 C<sub>6</sub>H<sub>6</sub>-EtOH, 0.23 g. exo-ferroceno [1.2] cyclohex-1-en-3-yl  $\alpha$ -phenylbutyrate (V). V was saponified with KOH-MeOH to give 40 mg. EtCHPhCO<sub>2</sub>H,  $[\alpha]_D^{19} 19 \pm 2^{\circ}$

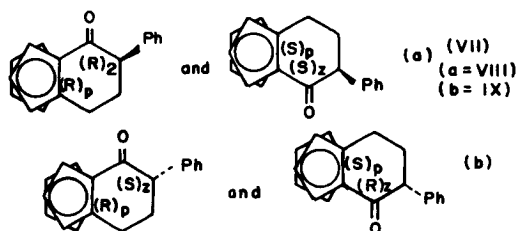
(c 2.6,  $C_6H_6$ ). The mixture of III and IV prepared according to Rinehart (R., et al., CA 57, 16650g) was chromatographed on alumina (100 g./1 g. ketone), eluting with  $C_6H_6$  to give IV, m. 158-60°,  $R_f$  0.38; or on Kieselgel, eluting with 15:1  $C_6H_6$ :EtOH to give III, m. 168-70°,  $R_f$  0.40. I (1.0 g.) in 20 ml. EtOH containing 0.4 g. NaOAc and 0.2 ml. HOAc was treated with 3.7 g. (—)-methydrizide, and refluxed 8 hrs. to give a mixture of mono- and bis-menthydrazones, which was taken up in  $H_2O$  and  $Et_2O$ , the aqueous phase extracted with  $Et_2O$ , and the combined  $Et_2O$  extracts washed, dried, and evaporated to give a residue which was separated by preparative chromatography, eluting with 15:1  $C_6H_6$ -EtOH. The low-mobility monohydrazone (0.5 g.) could not be crystallized but the bis (hydrazone) crystallized spontaneously to give 1.5 g., m. 138-9°,  $[\alpha]_D^{25}$  78  $\pm$  4° (c 0.275, EtOH). This was recrystallized four times to give, finally, 0.1 g. material, m. 148-9°,  $[\alpha]_D^{350}$  350°, which, in 0.5 ml. MeOH, was treated with 0.1 ml. 35 percent aqueous HCHO and three drops 85 percent  $H_3PO_4$  20 min. on a steam bath. The solution was diluted with  $H_2O$  and extracted with  $Et_2O$ , which was washed with  $H_2O$ ,  $NaHCO_3$ , and  $H_2O$ , evaporated in vacuo, and chromatographed, eluting with 15:1  $C_6H_6$ -EtOH to give 40 mg. I, m. 158-60°,  $[\alpha]_{578}^{20}$  110  $\pm$  2° (c 0.22, EtOH). IV (40 mg.) in 2 ml. absolute THF was refluxed with 20 mg.  $LiAlH_4$  30 min. at room temperature, and the mixture worked up as II above to give a mixture of three carbinols, of which the most mobile (endo-endo) appeared to be the main product. The mixture was dissolved in 2 ml.  $C_6H_6$  and shaken with 0.5 g. alumina (Woelm, acid, activity level I) 20 min. at 20°, and the absorbed material eluted with hexane to give bis (dihydroindenyl) iron (VI),  $[\alpha]_D^{25}$  -320  $\pm$  10° (c 0.25,  $C_6H_6$ ). VI was hydrogenated over Pd-C in EtOH to give inactive bis [1, 2:1', 2'- (tetramethylene)] ferrocene, m. 18-20°.

162. Falk, H. and Schlogel, K.,  
FERROCENE DERIVATIVES. XXV. FERROCENE  
ASYMMETRY, 4. THE ABSOLUTE CONFIGURATION OF  
( $\beta$ - AND  $\gamma$ -PHENYL- $\alpha$ -OXOTETRAMETHYLENE) FERRO-  
CENE, 5. THE APPLICATION OF A SEMI-EMPIRICAL  
METHOD OF CALCULATION TO OPTICALLY ACTIVE  
FERROCENE DERIVATIVES, Monatshefte fuer Chemie,  
Vol. 96, No. 3, 1965, pp. 1065-1093 (In German) (cf. CA 62,  
16025d).

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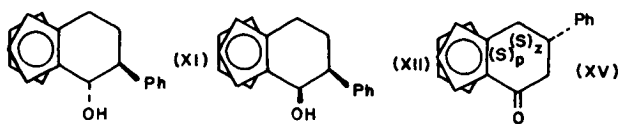
Fc = ferrocenyl throughout this abstract. Phenylsuccinic acid anhydride (17.9 g.) in 250 ml.  $\text{CH}_2\text{Cl}_2$  was added dropwise at  $20^\circ$  to 27 g.  $\text{AlCl}_3$  and 28 g. ferrocene (I) in 500 ml.  $\text{CH}_2\text{Cl}_2$  with stirring, the mixture stirred 2 hrs. at  $20^\circ$ , poured into ice- $\text{H}_2\text{O}$  containing some  $\text{Na}_2\text{S}_2\text{O}_6$ , the aqueous solution extracted with  $\text{CH}_2\text{Cl}_2$ , and the dried combined organic extracts were evaporated. The residue was treated with  $\text{KOHMeOH}$ , evaporated in vacuo, then taken up in  $\text{H}_2\text{O}$ , and the filtered alkaline solution was acidified with 1:1  $\text{HCl}$  and cooled, giving 95 percent of a mixture m.  $77-85^\circ$ , of  $\text{FcCOCH}_2\text{CHPhCO}_2\text{H}$  (II) and  $\text{FcCOCHPhCH}_2\text{CO}_2\text{H}$  (III). Because the Me esters of the mixture could not be separated by thin layer chromatography (TLC) on  $\text{Al}_2\text{O}_3$  or  $\text{SiO}_2$ , the mixture (24.5 g.) was refluxed 0.5 hr. with amalgamated Zn dust in 150 ml.  $\text{C}_6\text{H}_6$ ,  $\text{MeOH}$ ,  $\text{H}_2\text{O}$ , and concentrated.  $\text{HCl}$  and then methylated with  $\text{CH}_3\text{N}_2$ , giving 94 percent of a mixture of  $\text{FcCH}_2\text{CH}_2\text{CHPhCO}_2\text{Me}$  (IV) and  $\text{FcCH}_2\text{CHPhCH}_2\text{CO}_2\text{Me}$  (V) which was separated by chromatography with petr. ether on 1 kg.  $\text{Al}_2\text{O}_3$  to give 25 percent IV, m.  $130-1^\circ$ , and 22 percent V, m.  $115-17^\circ$  ( $\text{MeOH}$ ). IV did not give a crystalline brucine salt. Addition of 1.32 g. (—)  $\text{MeCHPhNH}_2$ ,  $[\alpha]_D -40^\circ$ , in  $\text{Et}_2\text{O}$  to 3.5 g. IV in 25 ml.  $\text{Et}_2\text{O}$  caused the separation of 96 percent amine salt,  $[\alpha]_D -18.7 \pm 1.5^\circ$  (c 0.7,  $\text{EtOH}$ ), from which on repeated crystallization from  $\text{EtOH}$  (+) -IV amine salt,  $[\alpha]_D 20^\circ$  ( $\text{MeOH}$ ), was obtained. Free (+) -IV had  $[\alpha]_D 67^\circ$  ( $\text{EtOH}$ ). (+) -IV (600 mg.),  $[\alpha]_D 35.5^\circ$ , was oxidized in 50 ml.  $\text{AcOH}$  with 1.6 g.  $\text{CrO}_3$  2 hrs. at  $20^\circ$ , the mixture evaporated in vacuo, the residue taken up in  $\text{H}_2\text{O}$  and extracted with  $\text{Et}_2\text{O}$ , giving a mixture of  $\alpha$ -phenylglutaric, phenylsuccinic, and phenyladipic acids, as shown by paper chromatography and mass spectrometry of the Me esters. Ring closure by treating 2 g. (+) -IV with

6 g.  $(\text{CF}_3\text{CO})_2\text{O}$  (VI) in 30 ml.  $\text{CCl}_4$ , stirring the mixture 1 hr. at  $0^\circ$  and 2 hrs. at  $20^\circ$ , pouring it into aqueous  $\text{NaHCO}_3$ , and extracting it with  $\text{CH}_2\text{Cl}_2$  gave 63 percent ( $\alpha$ -oxo- $\beta$ -phenyltetramethylene) ferrocene (ferrocene [1.2]-4-phenylcyclohexen-3-one) (VII), m.  $183-5^\circ$  (decomposition),  $R_f$  0.6 in TLC with 15:1  $\text{C}_6\text{H}_6$ -EtOH (Z refers to central and P to planar chirality). Prolonged treatment of IV with VI caused partial formation of the enol trifluoroacetate. On longer adsorption on the TLC plate, VII gave the isomeric ketone, m.  $154^\circ$ , which was also formed on cyclization of IV with (PO) for 3 days at  $20^\circ$ . Cyclization of 1.6 g. (+)-IV,  $[\alpha]_D^{20} 30^\circ$ , gave (—)-( $\alpha$ -oxo- $\beta$ -exo-phenyltetramethylene) ferrocene (VIII), m.  $185-210^\circ$  (decomposition),  $[\alpha]_D^{20} -276 \pm 2^\circ$  (c 0.45, EtOH or  $\text{C}_6\text{H}_6$ ), correct for optical purity (c. o. p.)  $-614 \pm 5^\circ$ . Isomerization of VIII on TLC plate gave the  $\beta$ -endo isomer (IX), m.  $150-70^\circ$ ,  $[\alpha]_D^{20} -103 \pm 2^\circ$  (c 0.5, all in  $\text{C}_6\text{H}_6$ ), c. o. p.  $-230^\circ$ . Reduction of 0.2 g. VIII,  $[\alpha]_D^{20} -135^\circ$ , in tetrahydrofuran (THF) with 40 mg.  $\text{LiAlH}_4$  and 130 mg.



$\text{AlCl}_3$  in  $\text{Et}_2\text{O}$  3 hrs. under reflux gave 23 percent (—)-( $\beta$ -exo-phenyltetramethylene) ferrocene (X),  $[\alpha]_D^{20} -11.5^\circ$  (c 3.02), c. o. p.  $-52^\circ$ . Reduction of 120 mg. VIII by refluxing with 12 g. amalgamated Zn dust as above gave 61 percent X, and similar reduction of 150 mg. VIII (o. p. 45 percent gave 130 mg. X, m.  $55-80^\circ$ ,  $[\alpha]_D^{20} -23.5^\circ$  (c 5.54), c. o. p.  $-52^\circ$ . VIII (350 mg.),  $[\alpha]_D^{20} -277^\circ$ , refluxed in THF with 0.1 g.  $\text{LiAlH}_4$  0.5 hr. followed by TLC ( $\text{C}_6\text{H}_6$ ) gave 291 mg. the endo carbinol (XI), m.  $88-107^\circ$ ,  $[\alpha]_D^{20} -85 \pm 2^\circ$  (c 6.77), c. o. p.  $-189^\circ$ , and 17 mg. exo carbinol (XII), m.  $90-112^\circ$ ,  $[\alpha]_D^{20} -93^\circ$  (c 1.11), c. o. p.  $-206^\circ$ . A mixture of XI and XII (250 mg.) was dehydrated with 3 g. acid  $\text{Al}_2\text{O}_3$  (Woelm, activity I) in 15 ml.  $\text{C}_6\text{H}_6$  and purified by TLC to give





65 percent (+)-ferroceno [1, 2]-4-phenylcyclohexa-1, 3-diene (XIII) as a reddish oil,  $[\alpha]_D^{25} 1010 \pm 5^\circ$  (c 1.9), c. o. p.  $2250^\circ$ . Hydrogenation of 114 mg. XIII with 1 percent Pd-C in EtOH gave 110 mg. (+)-( $\beta$ -endo-phenyltetramethylene) ferrocene (XIV), m.  $70-87^\circ$ ,  $[\alpha]_D^{25} -67^\circ$  (c 2.93), c. o. p.  $-149^\circ$ . Cyclization of V with VI gave 96 percent ( $\pm$ )-( $\alpha$ -oxo- $\gamma$ -phenyltetramethylene) ferrocene (XV), m.  $145-8^\circ$  (petr. ether), which (4.7 g.) was refluxed 2 hrs. with 5.5 g. (—)-menthylhydrazide,  $[\alpha]_D^{25} -75^\circ$ , to give 67 percent the menthylhydrazone, decomposing  $\sim 240^\circ$ ; it was repeatedly extracted with boiling EtOH to give a hydrazone with  $[\alpha]_D^{25} -654^\circ$  from which with HCHO and  $H_3PO_4$  80 percent (—)-XV, m.  $128-32^\circ$ ,  $[\alpha]_D^{25} -92^\circ$  (c 0.6), c. o. p.  $-128^\circ$ , was obtained. Reduction of 0.38 g. (—)-XV with  $LiAlH_4$  in THF gave (+)-( $\alpha$ -endo-hydroxy- $\gamma$ -endo-phenyltetramethylene) ferrocene (XVI),  $[\alpha]_D^{25} 36 \pm 0.8^\circ$  (c 2.8), c. o. p.  $50^\circ$ . Dehydration of XVI with  $Al_2O_3$  gave (+)-ferroceno [1, 2]-5-endo-phenylcyclohexa-1, 3-diene (XVII),  $[\alpha]_D^{25} 1560^\circ$ , c. o. p.  $2150^\circ$ . Hydrogenation of XVII with Pd-C gave  $\sim 100$  percent (+)-( $\beta$ -endo-phenyltetramethylene) ferrocene, m.  $92-9^\circ$ ,  $[\alpha]_D^{25} 109 \pm 2^\circ$  (c 3.76), with 72 percent o. p. The absolute configuration of these ketones was ascertained by correlation of the center of asymmetry of the dextrorotatory ( $R$ )<sub>p</sub> or the levorotatory enantiomer ( $S$ )<sub>2</sub> of the optically active V (the configuration of which had been primarily determined) with the configuration of the planar asymmetrical ( $R$ )<sub>p</sub> or ( $S$ )<sub>p</sub> portion in the optically active ketones VIII and IX. By determining the position of the Ph group in one of them relative to the ring plane, i. e. either exo as in VIII or endo as in IX, and since the configuration of ( $R$ )<sub>2</sub> or ( $S$ )<sub>2</sub> in (+)-IV is known, the absolute configuration of ( $R$ )<sub>2</sub> and ( $S$ )<sub>p</sub> can be unequivocally determined. The results are in agreement with those obtained earlier for (+)-1, 2-( $\alpha$ -oxotetramethylene) ferrocene and, in an independent way, by measurement of the optical dichroism.

## 5

The procedure of Brewster (CA 54, 9712e) was used for the calculation of the molecular rotation of optically active derivatives of 1, 2-tetramethyleneferrocene which have

asymmetric (chiral) centers in the cyclohexene moiety of the molecule in addition to the ferrocene asymmetry. Satisfactory agreement was obtained between the calculated and experimental observed values for the rotations. With carbinols XIX and XX the calculation of the absolute configuration of the planar asymmetrical portion was successful and was found to be in agreement with the results obtained by an independent



experimental method. The absolute conformation of some of the ferrocene derivatives is discussed on the basis of their optical circular dichroisms.

163. Furdik, M. and Toma, S.,  
DERIVATIVES OF FERROCENE VI. ACID-CATALYZED  
ALDOL CONDENSATION AND INTRAMOLECULAR  
MICHAEL CONDENSATION OF 1, 1'-DIACETYLFERRO-  
CENE AND O-CHLOROBENZALDEHYDE, Vol. 7, No. 10,  
1963, pp. 545-547 (In Slovak) (cf. 59, 1011a).

Refer to item No. 105 for abstract.

164. Furdik, M., Dzurilla, M., Toma, S., and Suchy, J.,  
DERIVATIVES OF FERROCENE. IX. SYNTHESIS OF NEW  
FERROCENECARBOXALDEHYDE DERIVATIVES, Acta Fac.  
Rerum Nat. Univ. Comenianae, Chimia, Vol. 8, No. 10,  
1964, pp. 569-579 (In Slovak) (cf. CA 61, 10706a).

To 15 cc.  $\text{Me}_2\text{CO}$  and 5 cc. 10 percent NaOH was added slowly (for 30 min.) 1.07 g. ferrocenecarboxaldehyde I in 15 cc.  $\text{Me}_2\text{CO}$ , the mixture stirred 2 hrs., and 50 cc.  $\text{H}_2\text{O}$  added to give 88 percent red ferrocenacetone, m.  $79-80^\circ$  (petr. ether). To 1.07 g. I, 0.45 g.  $\text{Me}_2\text{CO}$ , and 30 cc. EtOH was added slowly 5 cc. 10 percent NaOH and the mixture stirred 1 hr. to give 91 percent purple diferrocenacetone, m.  $205^\circ$  (petr. ether). A mixture of I (1.07 g.), 1.14 g. acetylferrocene, and 20 cc. MeOH was heated to  $45^\circ$ , 2.5 cc. 10 percent NaOH added within 1 hr. the mixture stirred at  $45^\circ$  under reflux 4 hrs., the precipitate filtered off, the filtrate concentrated and neutralized with dilute HCl, and

the precipitate filtered off, washed with  $\text{H}_2\text{O}$ , and added to the first product to give 46 percent purple ferrocenyl-ferrocene, m.  $205-6^\circ$  (dioxane). A mixture of Phthalide (0.65 g.), 1.07 g. I, 30 cc. absolute EtOH, and 1.5 g. Na was refluxed on a water bath 4 hrs., the solution evaporated in vacuo to 1/3 volume, the residue poured into 50 cc.  $\text{H}_2\text{O}$ , dilute HCl added to neutrality, and the precipitate filtered off and washed with ether to give 27 percent yellow 2-ferrocenyl-1, 3-indandione decomposed  $280^\circ$  (dioxane). The alkali-catalyzed aldol condensation of 2-ferrocenyl-1, 3-indandione was carried out as follows: to 1.07 g. I, 0.73 g. 1, 3-indandione, and 30 cc. EtOH was added 4 g. NaOH in 6 cc.  $\text{H}_2\text{O}$  and the mixture stirred at room temperature 5 hrs. to give red crystals of the nondehydrated aldolized products, carbonized at  $230^\circ$  without melting petr. ether-dioxane (1:2), and the Na salt dissolved in EtOH and acidified was dehydrated to 52.6 percent the expected 2-ferrocenyl-1, 3-indandione blue m.  $174^\circ$ . Acid-catalyzed aldol condensation: 1.07 g. I and 0.73 g. 1, 3-indandione in 15 cc. glacial AcOH was cooled to  $0-5^\circ$ , 15 cc. concentrated  $\text{H}_2\text{SO}_4$  added very slowly, the mixture stirred 1 hr., ice added, the mixture neutralized with NaOH solution, the reaction product extracted with  $\text{C}_6\text{H}_6$ , and the  $\text{C}_6\text{H}_6$  fraction dried with  $\text{MgSO}_4$  and evaporated in vacuo to give 76 percent blue crystals, m  $163-6^\circ$  (EtOH). Further recrystallization in  $\text{C}_6\text{H}_6$  and 5 percent petr. ether with silica gel and finally in EtOH yields 55.5 percent product, m.  $174^\circ$ . To a solution of 2.14 g. I and 1.4 g. 1, 1'-diacetylferrocene in 100 cc. MeOH was added slowly with constant stirring 5 cc. 10 percent NaOH at  $45-50^\circ$  and the mixture kept at this temperature with stirring 4 hrs. and 48 hrs. at room temperature to give red crystals which were washed with  $\text{H}_2\text{O}$  to give 41 percent yellow 1, 1'-( $\alpha$ ,  $\alpha'$ -dioxo- $\gamma$ -ferrocenylpentamethylene)-ferrocene (I), carbonized at  $300^\circ$ ; in a Kofler block at  $340^\circ$  I sublimed into needles, which immediately carbonized. Elementary analysis and infrared spectroscopy proved the structure and formulas of the compounds. The mechanisms of the reactions were described. The reactivity of the aldehyde radical of I is similar to that of benzaldehyde.

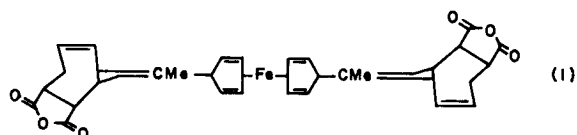
165. Furdik, M., Elecko, P., and Kovac, S.,  
DERIVATIVES OF FERROCENES. XI. SYNTHESIS OF  
HALO COMPOUNDS DERIVED FROM ACRYLOYLFERRO-  
CENES, Chemické Zvesti, Vol. 19, No. 5, 1965, pp. 371-  
378 (in Slovak) (cf. CA 61, 12033c).

By the addition of HCl, HBr, HI, or Br to the double bond of the acryloylferrocene (I) in CCl<sub>4</sub> in the cold,  $\beta$ -chloropropionylferrocene (II), dark orange-red m. 62.5-3.5°,  $\beta$ -bromopropionylferrocene (III), dark orange-red, m. 85.5-6.5°,  $\beta$ -iodopropionylferrocene (IV), brown-red, m. 93.5-4°, and  $\alpha$ ,  $\beta$ -dibromopropionylferrocene (V), dark-red, m. 150° (decomposition), were formed respectively. Also formed by the reaction directly from I, II, III, or from  $\beta$ -diethylaminopropionylferrocene-HCl, or by the condensation with p-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>NHNH<sub>2</sub> and cyclization, was 1-(p-nitrophenyl)-3-ferrocenyl-2<sup>2</sup>-pyrazoline (VI), red crystals with brown tinge, m. 167-8.5°. II, III, IV, and VI were determined chromatographically on silica gel. Characteristic frequencies of the ferrocene ring were determined in the region 1110 and 1015 cm.<sup>-1</sup> of all derivatives.

166. Furdik, M., Toma, S., Suchy, J., and Dzurilla, M.,  
DERIVATIVES OF FERROCENE. VII. DIELS-ALDER  
REACTION OF FERROCENYLFULVENE AND ITS DERI-  
VATIVES WITH N-SUBSTITUTED MALEIMIDES, Chemické  
Zvesti, Vol. 16, 1962, pp. 719-740 (cf. CA 58, 11398c).

Diels-Alder reaction of ferrocenylfulvene,  $\alpha$ -cyclopentadienylideneethylferrocene, and 1, 1'-bis ( $\alpha$ -cyclopentadienyldeneethyl)ferrocene with N-substituted maleimides and with maleic anhydride gave the following compounds (all endo isomers): anhydride of 7-ferrocenylmethylenebicyclo [1.2.2]-5-heptene-2, 3-dicarboxylic acid, yellow, m. 68-9.5°; N-methyl-7-ferrocenylmethylenebicyclo [1.2.2]-5-heptene-2, 3-dicarboximide, red-yellow, m. 171-3.5°; N-ethyl analog, orange, m. 159-60°; N-isopropyl analog, yellow-orange, m. 165.5-67°; N-allyl analog, yellow, m. 166-8°; N-butyl analog, red-brown, m. 132-3.5°; N-phenyl analog, yellow, m. 194-5°; anhydride of 7-methylferrocenylmethylenebicyclo [1.2.2]-5-heptene-2, 3-dicarboxylic acid, yellow, m. 159-62°; N-methyl-7-methylferrocenylmethylenebicyclo [1.2.2]-5-heptene-2, 3-dicarboximide, yellow, m. 162-4°, N-ethyl analog, yellow, m. 148-51°; N-isopropyl

analog, yellow, m. 142-5°; N-allyl analog, yellow, m. 155-8°; N-butyl analog, yellow, m. 125-7°; N-phenyl analog, yellow, m. 166-8°; I, yellow, m. 176-80°, N, N'-dimethyldicarboximide analog, yellow, m. 196-200°; N, N'-diethyl analog, yellow, m. 110-15°; N, N'-diisopropyl analog, yellow, m. 135-7°, (diene synthesis in Me<sub>2</sub>CO), m. 185-90° (diene synthesis in toluene); N, N'-diallyl analog, yellow, m. 171-4°; N, N'-di-butyl analog, yellow, m. 134-8°; N, N'-diphenyl analog, yellow, m. 180-2°, and when run in toluene, m. 247°. Only endo isomers were formed. Ferrocenealdehyde (81 percent yield) was prepared from ferrocene by a modification of Vilsmeier's formylation method. Crystalline ferrocenylfulvene was prepared, m. 59-60°, while Osgerby and Pauson (CA 56, 12939c) obtained it in the oily form.



167. Furdik, M., Toma, S., Suchy, J.,  
THE DERIVATIVES OF FERROCENE. V. ALDOL CONDENSATION OF 1, 1'-DIACETYLFERROCENE WITH ALIPHATIC ALDEHYDES, Chemické Zvesti, Vol. 16, 1962, pp. 449-457 (cf. CA 55, 18692e and CA 56, 7355a).

The aldol condensation of 1, 1'-diacetylferrocene with aliphatic aldehydes and consequent cyclization with intramolecular Michael addition was described. This reaction is similar to that of the basic catalyzed condensation of BzH and its derivatives with 1, 1'-diacetylferrocene and 1-acetyl-1'-acylferrocene but the yield is very much lower, from 9 to 18 percent. With HCHO, 1, 1'-( $\alpha$ ,  $\alpha'$ -dioxopentamethylene)ferrocene, yellow crystals, m. 253°, was formed; with AcH, 1, 1'-( $\alpha$ ,  $\alpha'$ -dioxo- $\gamma$ -methylpentamethylene) ferrocene, yellow needle crystals, m. 251.5-53°; with propionaldehyde, 1, 1'-( $\alpha$ ,  $\alpha'$ -dioxo- $\gamma$ -ethylpentamethylene) ferrocene, yellow crystals, m. 214.5-16.5°; with butyraldehyde, 1, 1'-[ $\alpha$ ,  $\alpha'$ -dioxo- $\gamma$ -propylpentamethylene] ferrocene, yellow crystals, m. 239-40°; with isobutyraldehyde, 1, 1'-( $\alpha$ ,  $\alpha'$ -dioxo- $\gamma$ -isopropylpentamethylene) ferrocene, yellow crystals, m. 269.5°, and with isovaleraldehyde, 1, 1'-( $\alpha$ ,  $\alpha'$ -dioxo- $\gamma$ -isobutylpentamethylene) ferrocene.

68. Gautheron, B., and Tirouflet, J.,  
HETEROBRIDGED KETONES DERIVED FROM FERROCENE,  
Comptes Rendus, Vol. 258, No. 26, 1964, pp. 6443-6445.

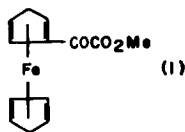
Refer to item No. 106 for abstract.

169. Goldberg, S. I. and Crowell, J. S.,  
MULTINUCLEAR FERROCENES. III. ACETYLATION OF  
BIFERROCENYL, Journal of Organic Chemistry, Vol. 29,  
No. 5, 1964, pp. 996-1000 (cf. CA 60, 6864c).

Acetylation of biferrocenyl with  $\text{Ac}_2\text{O}$  in the presence of polyphosphoric acid provides all three possible mono-acetylbiferrocenyl position isomers as well as three isomeric diacetylbiferrocenyls. Structure assignments for all products are made on the basis of nuclear magnetic resonance analysis, while previous infrared and ultraviolet spectral correlations for disubstituted ferrocenes are examined. In spite of the fact that the ferrocenyl group has been established as a strong electron donor, competitive acetylation of ferrocene and biferrocenyl in the present work shows that biferrocenyl is less susceptible to electrophilic substitution than is ferrocene. This apparent inconsistency is explicable in terms of a rapid equilibrium in which the iron atom of one ferrocene nucleus in biferrocenyl is bonded to electrophile, thus deactivating the molecule.

170. Goldberg, S. I. and Keith, L. H.,  
SYNTHESIS OF METHOXALYLFERROCENE, Journal of Chemical and Engineering Data, Vol. 9, No. 2, 1964,  
pp. 250-251 (Correction of CA 61, 3147c).

Methoxalylferrocene (I) was prepared by treatment of Me ferrocenylacetate with  $\text{MnO}_2$  at room temperature.



171. Huffman, J. W. and Rabb, D. J.,  
1, 2-( $\alpha$ -OXOTETRAMETHYLENE) FERROCENE, Journal  
of Organic Chemistry, Vol. 26, 1961, pp. 3588-3589.

The title compound (I) (previously reported by Rinehart and Curby, CA 51, 16442h) was prepared by a modified procedure, since hydrogenation of the intermediate  $\beta$ -ferrocenoylpropionic acid (II) to  $\gamma$ -ferrocenylbutyric acid (III) failed repeatedly except in one instance where an exhaustively purified sample of II was used. In the latter case, a drastically reduced overall yield of I resulted. From 20.0 g. ferrocene, 7.08 g. succinic anhydride, and 15.6 g.  $\text{AlCl}_3$  was obtained 18.5 g. crude II, m.  $167-9^\circ$ . To 13.6 g. II in 635 ml. iso-PrOH was added 32.0 g.  $\text{NaBH}_4$ , the mixture refluxed 2 hrs., cooled, diluted with  $\text{H}_2\text{O}$ , filtered through Celite, the filtrate acidified with dilute  $\text{HCl}$ , extracted with  $\text{CHCl}_3$ , the combined extracts washed with  $\text{H}_2\text{O}$  and 5 percent aqueous  $\text{Na}_2\text{CO}_3$ , dried, concentrated in vacuo, and the residue (12.7 g.) recrystallized from cyclohexane-EtOAc to give 9.3 g.  $\gamma$ -ferrocenylbutyrolactone (IV), m.  $132-3^\circ$  (cyclohexane),  $\lambda$  (Nujol)  $5.66 \mu$ . IV (10.6 g.) in 218 ml. AcOH containing 2.0 g.  $\text{PtO}_2$  hydrogenated 16 hrs. at 50 psi and room temperature, filtered through Celite, the filtrate diluted with  $\text{H}_2\text{O}$ , treated with sufficient ascorbic acid to discharge the green color present, extracted with  $\text{CHCl}_3$ , the  $\text{CHCl}_3$  solution washed with  $\text{H}_2\text{O}$ , extracted with 10 percent aqueous  $\text{Na}_2\text{CO}_3$ , and the combined extracts acidified gave 9.8 g. III, m.  $115-17^\circ$ . III (9.8 g.) and 150 g. polyphosphoric acid kept 2.5 hrs. at room temperature with occasional stirring, the mixture poured into  $\text{H}_2\text{O}$ , kept several hrs., extracted with  $\text{CHCl}_3$ , the combined extracts washed with  $\text{H}_2\text{O}$  and 5 percent aqueous  $\text{Na}_2\text{CO}_3$ , dried, and evaporated in vacuo gave 4.04 g. I, m.  $83-5^\circ$  (hexane),  $\lambda$  ( $\text{CCl}_4$ )  $6.03 \mu$ .

172. Leigh, T.,  
FERROCENE DERIVATIVES, British Patent 898,633, 14  
June 1960, Applied 27 January 1960, 4 pp., Addendum to  
British Patent 819,108 (CA 54, 7732b).

Refer to item No. 139 for abstract.

173. Little, W. F., Lynn, K. N., and Williams, R.,  
A NOVEL SIDE REACTION ACCOMPANYING THE ARYLATION OF FERROCENE. AN EXAMPLE OF FREE RADICAL SUBSTITUTION, American Chemical Society Journal, Vol. 85, No. 19, 1963, pp. 3055-3056.

In the reaction of certain o-substituted diazonium salts with ferrocene (FeH) in  $\text{CH}_2\text{Cl}_2$  solution, significant amounts of FeCHO were formed. It was shown that electronic and steric effects of the substituents caused preferential reaction with the solvent. Reactions of FeH with: o-toluenediazonium acetate (I) in  $\text{CH}_2\text{Cl}_2$  gave 16 percent FeCHO; mesitylenediazonium acetate in  $\text{CH}_2\text{Cl}_2$  gave 23 percent FeCHO; I in  $\text{CHCl}_3$  gave 25 percent  $\text{FeCO}_2\text{H}$ ; 2, 6-dimethylbenzenediazonium fluoroborate (II) in  $\text{CHCl}_3$  gave 26 percent  $\text{FeCO}_2\text{Et}$ ; II in  $\text{MeCHCl}_2$  gave 10 percent  $\text{FeCOMe}$ ; o-toluenediazonium fluoroborate in  $\text{MeCHCl}_2$  gave 5 percent  $\text{FeCOMe}$  and 64 percent o- $\text{MeC}_6\text{H}_4\text{Fe}$ ; and 2, 6-dimethylbenzenediazonium acetate in  $\text{CCl}_3\text{Br}$  gave 43 percent  $\text{FeCO}_2\text{H}$ . The formation of the aldehyde is explained as an attack of the dichloromethylradical on the FeH nucleus, followed by hydrolysis.

174. Lorkowski, H. J.,  
FERROCENE DERIVATIVES. III. THE SYNTHESIS OF METHOXY- AND HYDROXYARYLFERROCENES, Journal fuer Praktische Chemie, Vol. 27, No. 1-2, 1965, pp. 6-17 (In German) (cf. CA 60, 13269c).

The synthesis of the title compounds was examined systematically for those which might be suitable for polymer preparations. 1, 1'-Dihydroxyferrocene was unsuitable because of its instability and sensitivity to air.  $\text{LiAlH}_4$  in  $\text{Et}_2\text{O}$  was added dropwise to chloroacetylferrocene in aqueous  $\text{Et}_2\text{O}$  and the solution refluxed 1 hr. under N and worked up to give  $\alpha$ -hydroxy- $\beta$ -chloroethylferrocene, m.  $76-7^\circ$  ( $\text{C}_6\text{H}_{14}$ ). A solution of ferrocene in concentrated  $\text{H}_2\text{SO}_4$  was kept 8 hrs. poured over ice, and the diazonium sulfate from 33 g. o-anisidine added dropwise. After 4 hrs. at room temperature, the filtrate from this mixture was reduced with Zn dust, then shaken with  $\text{Et}_2\text{O}$ . The product recovered from the  $\text{Et}_2\text{O}$  consisted of o-anisylferrocene (m.  $58^\circ$ ) and 1, 1'-di-o-anisylferrocene (m.  $99^\circ$ ). p-Anisylferrocene and  $\text{MeMgI}$  was heated to  $200^\circ$  under N, and the product ground up,



mixed with 2N  $\text{H}_2\text{SO}_4$ , and worked up to give p-hydroxyphenylferrocene, m.  $161-3^\circ$ , which, treated with an EtOH solution of allyl bromide containing EtONa, gave p-ferrocenylphenyl allyl ether (m.  $110-11^\circ$ ). A solution of 3, 4-dimethoxybenzoic acid in  $\text{CH}_2\text{Cl}_2$  was cooled to  $-30^\circ$ ,  $\text{AlCl}_3$  added, ferrocene in  $\text{CH}_2\text{Cl}_2$  added dropwise, and the mixture kept  $\sim 18$  hrs. and worked up to give 3, 4-dimethoxybenzoylferrocene, m.  $55-6^\circ$ . Also prepared were 1, 1'-bis (p-hydroxyphenyl) ferrocene (decomposed  $220^\circ$ ), 3, 4-dimethoxyphenylferrocene (m.  $105-6^\circ$ ), 1, 1'-bis (3, 4-dimethoxyphenyl)ferrocene (m.  $140-2^\circ$ ), 3, 4-dihydroxybenzoylferrocene (m.  $161-3^\circ$ ), 3, 4-dimethoxybenzoylferrocene (m.  $90-1^\circ$ ), hydroxymethylferrocene p-nitrobenzoate (m.  $164-5^\circ$ ), and hydroxymethylferrocene p-aminobenzoate (m.  $147-8^\circ$ ).

175. Nakamura, A.,

DIENE COMPLEXES OF TRANSITION METALS. MECHANISMS FOR CYCLIC POLYMERIZATION OF ACETYLENIC COMPOUNDS, Mem. Inst. Sci. Ind. Res., Osaka Univ., Vol. 19, 1962, pp. 81-95.

Cyclopentadienyl (methyl) iron carbonyl (I) and  $\text{PhC}:\text{CPh}$  (II) gave  $\sim 10$  percent 1, 2, 3, 4-tetraphenylferrocene, m.  $226^\circ$ ; I and  $\text{HC}:\text{CH}$  gave ferrocene. Ethyliron (III) and benzyliron analogs of I did not give the corresponding ferrocene compounds but instead gave hexaphenylbenzene and many other products. I and  $\text{MeC}:\text{CMe}$  gave unexpectedly ferrocene. Cyclopentadienyl (methyl) molybdenum tricarbonyl (IV) and II gave a tetraphenyl substituted cyclopentadiene (V) and a diphenylacetylene complex of Mo (VI) as well as other products; V was not identical with the product described by Wislicenus and Carpenter (Ann. Vol. 302, 1898, p. 223); VI and Na in liquid  $\text{NH}_3$  gave  $(\text{PhCH}_2)_2$ . II with either cyclopentadienylmolybdenum tricarbonyl hydride or bis (cyclopentadienylmolybdenum) hexacarbonyl also gave VI. IV and  $\text{PhC}:\text{CH}$  gave a phenylacetylene complex related to VI, m.  $138-9^\circ$ . IV and  $\text{HC}:\text{CH}$  gave a black polymer of  $\text{HC}:\text{CH}$ . III and II gave methyltetraphenylcyclopentadiene, m.  $180-1^\circ$ , and 1, 2, 3, 4-tetraphenylbenzenecyclopentadienylmolybdenum, m.  $207^\circ$ . Possible mechanisms for the formation of cyclooctatriene by cyclic dimerization of  $\text{HC}:\text{CH}$  are discussed.

176. Nesmeyanov, A. N., Kochetkova, N. S., Vil'chevskaya, V. D., Sheinker, Y. N., Senyavina, L. B., and Struchkova, M. I., o-CARBOXY- AND o-HYDROXYBENZOYLFERROCENES AND THEIR DERIVATIVES, Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, 1962, pp. 1990-1996 (cf. CA 55, 21080c).

Ferrocene and salicylyl chloride in  $\text{CH}_2\text{Cl}_2$ - $\text{Et}_2\text{O}$  in the presence of  $\text{AlCl}_3$  0.5 hr. at  $45$ - $50^\circ$  gave after an aqueous treatment 22 percent o-salicylylferrocene (I), red crystals, m.  $87.5$ - $8^\circ$ , after chromatographic purification on  $\text{SiO}_2$  and elution with  $\text{C}_6\text{H}_6$ ; 2, 4-dinitrophenylhydrazine, violet, m.  $214$ - $14.5^\circ$ . I and amalgamated Zn in  $\text{AcOH-HCl}$  gave o-hydroxybenzylferrocene, m.  $82.5$ - $3.5^\circ$ , which with  $\text{Me}_2\text{SO}_4$  in  $\text{MeOH-KOH}$  gave 94 percent yellow o-methoxybenzylferrocene, m.  $53.5$ - $4.5^\circ$ . Similar methylation of I gave o-methoxybenzoylferrocene, m.  $135^\circ$ . I and  $\text{Ac}_2\text{O}$  5 days gave 95 percent o-acetoxybenzoylferrocene, m.  $120$ - $20.5^\circ$ , which was saponified with 30 percent  $\text{KOH}$  to I. I and  $\text{LiAlH}_4$  gave 90 percent o-hydroxyphenylferrocenylcarbinol (II), m.  $83.5$ - $4.5^\circ$  (with decomposition) which gradually darkened in air; treated with  $\text{Me}_2\text{SO}_4$  in  $\text{KOH}$  it gave 93 percent o-methoxyphenylferrocenylcarbonyl Me ether, m.  $113$ - $14^\circ$ . Simple crystallization of II from  $\text{ROH}$  gave  $\text{C}_{10}\text{H}_9\text{FeCH(OR)-C}_6\text{H}_4\text{OH-o}$  (R shown): Me, m.  $119$ - $20^\circ$ ; Et, m.  $117^\circ$ ; and iso-Pr, m.  $79$ - $80^\circ$ . Infrared spectra of the products are shown. These indicated that I possesses internal hydrogen bonds of chelate nature between the carbonyl and HO groups.

177. Nesmeyanov, A. N., Perevalova, E. G., and Beinoravichute, Z. A., REDUCTION OF FERROCENECARBOXYLIC ACIDS, Doklady Akademii Nauk SSSR, Vol. 112, 1957, pp. 439-440.

To PhNa (from 10 g. Na and 21 g.  $\text{PhCl}$ ) in  $\text{C}_6\text{H}_6$  was added 18.6 g. ferrocene, the mixture kept overnight, refluxed 8 hrs., poured on dry ice, steam-distilled to remove  $\text{BzOH}$ , and the ferrocenedicarboxylic acid dried in air and extracted with hot  $\text{C}_6\text{H}_6$  to remove traces of ferrocenemonocarboxylic acid; 55 percent ferrocene was recovered. The yield of ferrocenedicarboxylic acid was 42 percent on ferrocene used and 94 percent on reacted ferrocene. Heating its di-Me ester (2 g.) with excess  $\text{LiAlH}_4$  gave 92 percent bis (hydroxymethyl) ferrocene, m.  $85$ - $6^\circ$  (from  $\text{EtOH}$  or  $\text{Et}_2\text{O}$ -petr. ether).

If the ester (2 g.) is heated in Et<sub>2</sub>O as above but with twice the amount of LiAlH<sub>4</sub> (prepared from 1.2 g. LiH) it yields 89 percent 1, 1'-dimethylferrocene, m. 29-30° (from EtOH). Reduction with LiAlH<sub>4</sub> of Me ferrocenemonocarboxylate gave 73 percent ferrocenecarbinol, m. 74-5°, purified by adsorption on Al<sub>2</sub>O<sub>3</sub> and crystallization from Et<sub>2</sub>O-petr. ether. Reduction of 1, 1'-bis (diphenylhydroxymethyl)-ferrocene with LiAlH<sub>4</sub> gave 87 percent 1, 1'-dibenzhydryl-ferrocene, m. 161-2° (cf. CA 49, 5454i). Treatment of di-Me ferrocenedicarboxylate with PhMgBr or reaction of Ph<sub>2</sub>CO with dilithiumferrocene gave bis (diphenylhydroxymethyl) ferrocene, m. 179-80° (cf. Riemschneider and Helm, CA 50, 15436b). Reduction of 1,1'-dibenzoylferrocene as above with LiAlH<sub>4</sub> gave 87 percent dibenzylferrocene (cf. Nesmeyanov and Vol'kenau, CA 50, 15519h).

178. Nesmeyanov, A. N., Perevalova, E. G., and Grandberg, K. I., SYNTHESIS OF SOME HETEROANNULAR SUBSTITUTED FERROCENECARBOXYLIC ACIDS, Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 10, 1964, pp. 1903-1905 (In Russian).

Reaction of chloroferrocene with HCN in the presence of FeCl<sub>3</sub> in tetrahydrofuran (THF) (CA 55, 4464c for details) gave 79 percent chloroferrocenecarbonitrile (I), m. 100.5-1.5°, with heteroannular substituents as confirmed by the infrared spectrum. Heating 7 g. Me ferrocenecarboxylate in THF with 30 g. FeCl<sub>3</sub> in 80 ml. THF and 20 ml. liquid HCN to reflux, followed by 12 hrs. at room temperature, gave 90 percent Me 1-cyano-1'-ferrocenecarboxylate (II), m. 96.5-7.5°. I refluxed 8 hrs. with alcoholic KOH gave 78 percent 1-chloro-1'-ferrocenecarboxylic acid, decomposed 174-6°. Similarly was prepared 89 percent 1-bromo-1'-ferrocenecarboxylic acid, m. 163.5-4.5°. Heating II with NaOH in aqueous MeOH 1 hr. gave 85 percent 1-cyano-1'-ferrocenecarboxylic acid, m. 178-80° (decomposition). 1-Acetoxy-1'-ferrocenecarboxylic acid in EtOH was treated with Me<sub>2</sub>SO<sub>4</sub>, heated and treated with 50 percent KOH and refluxed 1 hr.; acidification gave 88 percent 1-methoxy-1'-ferrocenecarboxylic acid, m. 139.5-40.5°, which with CH<sub>2</sub>N<sub>2</sub> gave the Me ester, m. 37.5-39°. Me 1-bromo-1'-ferrocenecarboxylate, m. 68.5-9.5°.

179. Nesmeyanov, A. N., Perevalova, E. G., Yur'eva, L. P., and Grandberg, K. I.,  
SYNTHESIS OF FERROCENE DERIVATIVES FROM NITRILES OF FERROCENECARBOXYLIC ACIDS, Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 8, 1963, pp. 1377-1380 (cf. CA 58,7971h).

Ferrocenenyl cyanide (I) refluxed 3 hrs. in aqueous EtOH-NaOH, then 4 hrs. with fresh alcoholic NaOH gave 80 percent ferrocenecarboxylic acid, decomposed 196-210°; Me ester m. 69.5-70.5°. Heating I with EtOH in the presence of concentrated H<sub>2</sub>SO<sub>4</sub> (11 hrs.) gave 14 percent ferrocenecarboxamide (II), m. 165-8°, 47 percent Et ferrocenecarboxylate, m. 59-60°, and 8 percent unreacted I, m. 105-7°; these were separated by chromatography on Al<sub>2</sub>O<sub>3</sub> by elution with petr. ether-C<sub>6</sub>H<sub>6</sub> for I and Et ester, and with Et<sub>2</sub>OCHCl<sub>3</sub> for the amide. Heating I at 40° with EtOH and 50 percent KOH while adding 3 percent H<sub>2</sub>O<sub>2</sub> (10 min.) gave 93 percent II. I in absolute EtOH was treated with Na to give after 1 hr. of heating, followed by acidification, 48 percent II. Reduction of I in tetrahydrofuran with LiAlH<sub>4</sub> gave 74 percent ferrocenylmethylamine, b<sub>1</sub> 109-11°, n<sub>D</sub><sup>20</sup> 1.6260; HCl salt m. 233-5°; picrate decomposed 160-70°. I in CHCl<sub>3</sub> added to SnCl<sub>2</sub> in Et<sub>2</sub>O saturated with dry HCl, heated 4 hrs., and kept 12 hrs. at room temperature (this process being repeated three times) gave 40 percent unreacted I and 14 percent ferrocenecarboxaldehyde, m. 116-17°, purified on Al<sub>2</sub>O<sub>3</sub> (elution with C<sub>6</sub>H<sub>6</sub>). 1, 1'-Dicyanoferrocene hydrolyzed with NaOH in aqueous EtOH gave 34 percent ferrocene-1,1'-dicarboxylic acid; di-Me ester m. 114-15°.

180. Nesmeyanov, A. N., Vil'chevskaya, V. D., and Kochetkova, N. S.,  
SYNTHESIS OF 1-FERROCENOYL-2-CARBOMETHOXY-ETHYLENE, Doklady Akademii Nauk SSSR, Vol. 152, No. 3, 1963, pp. 627-628.

Ferrocene in CH<sub>2</sub>Cl<sub>2</sub> was treated with 1 mole carbomethoxymalcoyl chloride in the presence of 1 mole AlCl<sub>3</sub> in Et<sub>2</sub>O; after 1.5 hrs. refluxing, followed by quenching in ice, it gave deep violet 1-ferrocenoyl-2-carbomethoxyethane (I), m. 99.5-100°, purified on Al<sub>2</sub>O<sub>3</sub> in petr. ether. The same reactants in CS<sub>2</sub>-Et<sub>2</sub>O solution gave β-carboxypropionylferrocene m. 167°; the use of 2

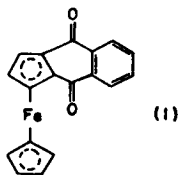
moles acyl chloride resulted in this case in formation of 22 percent 1, 1'-bis (1-oxo-2-carbomethoxyethenyl) ferrocene, m. 164°. Hydrogenation of I over Pt in EtOH gave  $\beta$ -carbomethoxypropionylferrocene, m. 60°.

181. Nesmeyanov, A. N., Vol'kenau, N. A., Vil'chevskaya, V. D., Woodward, et al.,  
INTRAMOLECULAR ACYLATION IN THE FERROCENE SERIES, Doklady Akademii Nauk SSSR, Vol. 111, 1956, pp. 362-364 (cf. CA 50, 15519h and CA 48, 2053g).

Reaction of ferrocene with phthalic anhydride in the presence of  $AlCl_3$  gave bis (o-carboxybenzoyl) ferrocene and some o-carboxybenzoylferrocene, orange, infusible solid, which converted to the Na salt and treated with  $Me_2SO_4$  gave o-carbomethoxybenzoylferrocene, m. 134-5° (from heptane). Ferrocene (0.024 mole) with 0.048 mole  $(CH_2CO)_2O$  and 0.097 mole  $AlCl_3$  in  $CS_2$  gave bis (3-carboxypropanoyl) ferrocene (I), orange, m. 165° (from 50 percent MeOH), in which the substituents are probably in different rings by analogy with other diacylferrocenes. Attempts to cyclize this substance with  $H_2SO_4$  or polyphosphoric acid failed. Reduction of 3 g. of this acid by Clemmensen method with 10 g. Zn-Hg in AcOH-HCl gave in 1.5 hrs. yellow bis (3-carboxypropyl) ferrocene (II), 77 percent m. 109.5-10.5° (from  $C_6H_6$ -petr. ether). This (1 g.) heated 4 hrs. in polyphosphoric acid gave a red product of cyclization,  $C_{18}H_{18}O_2Fe$ , m. 130° (from  $C_6H_6$ -petr. ether), forming an orange dioxime, decomposes 160° (from dioxan $\bar{e}$ ). The diketone probably contains 2-cyclohexanonyl rings fused to each of the cyclopentyl rings of ferrocene, since Clemmensen reduction of this substance gave some 50 percent bis (tetrahydroindenyl) iron, orange-red, m. 19.5-20.5°,  $b_{0.001}$  126°, readily oxidized by air,  $\lambda_{max}$ . 4350 and 3250 A.  $\lambda_{min}$ . 3650 and 3200 A. (cf. Fischer and Seus, CA 48, 7475c). Ferrocene (0.026 mole) with 0.052 mole 3-carbomethoxypropanoyl chloride in the presence of  $AlCl_3$  in  $CS_2$  gave 27 percent bis (3-carbomethoxypropanoyl) ferrocene, orange, m. 98°, which did not cyclize with polyphosphoric acid; with aqueous KOH this gave the dicarboxy analog, decomposes 165°, identical with I. Clemmensen reduction of the di-Me ester gave II when run in acid medium; run in MeOH, the reaction gave orange bis (3-carbomethoxypropyl) ferrocene,  $b_{0.0001}$  148°, m. 16.5-17.5°.

182. Nesmeyanov, A. N., Vil'chevskaya, V. D., Kochetkova, N. S., and Gorelikova, Y. Y.,  
FERROCENEANTHRAQUINONE, USSR Patent 176,923  
(Cl. C 07) 1 December 1965, Applied 19 March 1965. (Byul. Izobret. i Tovarnykh Znakov, No. 24, 1965, pp. 26-27).

The title compound (I) is prepared by treating



ferroceneanthrone with  $\text{MnO}_2$  suspended in  $\text{C}_6\text{H}_6$ . A product suitable for dyeing wool, silk, and synthetic fibers is thus obtained.

183. Nesmeyanov, A. N., Vol'kenau, N. A., Woodward, et al.,  
ACYLATION OF ACETYL- AND ETHYLFERROCENES,  
Doklady Akademii Nauk SSSR, Vol. 111, 1956, pp. 605-608  
(cf. CA 50, 15519h and CA 48, 2053g).

Reaction of 3 g. acetylferrocene (I), 1 g.  $\text{AcCl}$ , and 3.39 g.  $\text{AlCl}_3$  in  $\text{CS}_2$  0.5 hr. at room temperature and 0.5 hr. at reflux gave 89 percent 1, 1'-diacetylferrocene, m.  $130-1^\circ$ , identical with that from ferrocene and  $\text{AcCl}$ . Similarly, I and  $\text{BzCl}$  gave 48 percent 1-acetyl-1'-benzoylferrocene, m.  $71-2^\circ$ . Ethylferrocene (4 g.) and 2.81 g.  $\text{AcCl}$  with 4.82 g.  $\text{AlCl}_3$  in  $\text{CS}_2$  similarly gave 68 percent red oily diacetylethylferrocene, which, after purification by adsorption on  $\text{Al}_2\text{O}_3$ , gave a disemicarbazone, decompose  $208-10^\circ$ , with 10 percent x-ethyl-1-acetylferrocene, red liquid, whose semicarbazone, m.  $189-91^\circ$ . Refluxing 60 ml.  $\text{AcOH}$ , 6.12 g.  $\text{SiCl}_4$ , and 120 ml.  $\text{C}_6\text{H}_6$  3 hrs., followed by addition of 8 g. ethylferrocene in 8 ml.  $\text{C}_6\text{H}_6$  and slow addition of 18.8 g.  $\text{SnCl}_4$  in  $\text{C}_6\text{H}_6$  and refluxing 4 hrs. gave 5 g. mixed oily ketones which after purification on  $\text{Al}_2\text{O}_3$  still gave mixed isomeric acetylethylferrocenes (II) as well as 8 percent diacetylethylferrocene (disemicarbazone, m.  $208-9^\circ$ ). II gave semicarbazones, m.  $141-2^\circ$  and  $190-2^\circ$  in 1:3 ratio. The former semicarbazone reduced with

Zn-AcOH gave 01 percent 1, x-diethylferrocene,  $n_D^{20}$  1.5761,  $d_{20}$  1.1655, while the second semicarbazone gave 1, 1'-diethylferrocene. Similar reduction of diacetylethylferrocene gave 56 percent triethylferrocene,  $n_D^{20}$  1.5613,  $d_{20}$  1.1201. Treatment of 1 g. ethylferrocene in  $CCl_4$  with 6.4 g. Br gave a vigorous reaction yielding, after refluxing 1 hr., 74 percent pentabromocyclopentane, m. 102-3°, also formed on bromination of 1, x-diethylferrocene. Thus, ferrocene shows lesser activity of the ring in which an Ac group is located, while the Et-substituted ring is more reactive than that in unsubstituted ferrocene.

184. Palitsyn, N. P., Nesmeyanov, A. N., Vil'chevskaya, V. D., and Kochetkova, N. S.,  
WATER-SOLUBLE SALTS OF o-CARBOXYBENZOYLFERROCENE, USSR Patent 179,309 (Cl. C 07f), 8 February 1966, Applied 3 November 1964 (Izobret., Prom. Obraztsy, Tovarnye Znaki, Vol. 43, No. 5, 1966, p. 21).

For obtaining antianemia preparations, o-carbomethoxybenzoylferrocene is heated with metal hydroxides or alcoholates.

185. Pavlik, I. and Zizek, V.,  
ACETYLFERRICINIUM SALTS, Collection of Czechoslovak Chemical Communications, Vol. 31, No. 5, 1966, p. 1985.

Refer to item No. 27 for abstract.

186. Rai, C.,  
DERIVATIVES OF FERROCENE, U. S. Patent 3,222,373 (Cl. 260-299), 7 December 1965, Applied 6 June 1963, 3 pp.

The title compounds which have utility as scintillating agents and ultraviolet light absorbers were prepared by acylating ferrocene (I) with an alkyl or aryl anhydride to form the oxo acid, reducing the latter to the corresponding mono- or dicarboxylic acid, and condensing the acid with an o-hydroxy, o-mercapto, or o-aminoaryl amine in the presence of polyphosphoric acid (II) catalyst. Thus,  $CH_2Cl_2$  (200 cc.) and 11.6 g.  $AlCl_3$  was added slowly to 9.29 g. I and 11 g. succinic anhydride, the mixture was stirred 2 hrs. and poured into ice to yield 4 g.  $\beta$ -ferrocenoylpropionic acid (III), m. 168°. III was hydrogenated in 250 cc. AcOH over

950 mg. Pt oxide under 30 psig. H for 48 hrs. and worked up in the conventional manner to yield 3.45 g.  $\gamma$ -ferrocenylbutyric acid (IV), m. 116°. IV (2.72 g.) and 1.5 g. o-aminothiophenol were added slowly to 50 g. II which was heated to 100°. The mixture was heated and stirred 2 hrs., cooled, and poured into ice, to precipitate 2.5 g. 1-(2-benzothiazolyl) propylferrocene, m. 108°. A number of similar I derivatives are listed.

187. Rausch, M. D. and Coleman, L. E., Jr.,  
DERIVATIVES OF FERROCENE. IV. FERROCENE-  
CONTAINING UNSATURATED KETONES, Journal of Organic Chemistry, Vol. 23, 1958, pp. 107-108.

In a study of vinyl polymers containing the ferrocene ban, cinnamoylferrocene (I) was synthesized and the preparation of ferrocenyl vinyl and isopropenyl ketones (II, III) was attempted. Ferrocene (IV) (65.2 g.) in 300 ml.  $\text{CH}_2\text{Cl}_2$  stirred (N atmosphere) with addition of 46.7 g. anhydrous  $\text{AlCl}_3$  and 58.4 g. trans- $\text{PhCH:CHCOCl}$  in 300 ml. dry  $\text{CH}_2\text{Cl}_2$  with evolution of HCl, the blue-green mixture stirred 22 hrs. at room temperature treated with 500 g. ice, the light-blue aqueous phase extracted twice with 50 ml.  $\text{CCl}_4$ , the extract washed to neutrality with 100 ml. portions of  $\text{H}_2\text{O}$ , the dried ( $\text{CaSO}_4$ ) extract evaporated, the red crystalline residue taken up in 400 ml. hot 95 percent alcohol, the solution kept overnight at -20°, filtered, and the product dried yielded 81.5 percent I, m. 139.5-9.7°. Acetylferrocene (V) (2.18 g.) and 1.06 g. BzH shaken 40 hrs. at room temperature with 5 ml. 10 percent NaOH and 30 ml. MeOH and the solvent evaporated gave 47 percent crude I, m. 130-1°, recrystallized (MeOH) to give material, m. 139.0-9.5°; oxime, m. 116-18°; recrystallized (MeOH) to give material, m. 139.0-9.5°; oxime, m. 116-18°. The Friedel-Crafts procedure is preferable to the Claisen-Schmidt condensation. I in BuOH hydrogenated with 5 percent Pt-C yielded 57 percent material, m. 81.5-2.5°; recrystallized (alcohol) to give ( $\beta$ -phenylpropionyl) ferrocene, m. 84.5-4.8°. IV (57.7 g.) in  $\text{CH}_2\text{Cl}_2$  treated with 27.8 g.  $\text{EtCOCl}$  and 4.0 g. anhydrous  $\text{AlCl}_3$  in  $\text{CH}_2\text{Cl}_2$  and hydrolyzed as above, the product worked up, the dark oily residue chromatographed on  $\text{Al}_2\text{O}_3$ , the column eluted with  $\text{CHCl}_3$ , and the fraction crystallized (petr. ether) produced 34.8 g. propionylferrocene (VI), m. 38.0-8.2°; oxime, m. 135.4-36° (50 percent alcohol). V (11.4 g.), 4.08



g.  $\text{NHMe}_2 \cdot \text{HCl}$ , 2.25 g. paraformaldehyde, 0.15 ml. concentrated  $\text{HCl}$ , and 50 ml. absolute alcohol refluxed 1 hr. and treated with 1.50 g. paraformaldehyde, the mixture refluxed 2 hrs., the cooled mixture evaporated, the residue extracted repeatedly with  $\text{Et}_2\text{O}$  to give 7.1 g. V, and the insoluble residue recrystallized (alcohol-EtAc) yielded 68 percent ( $\beta$ -dimethylaminopropionyl) ferrocene  $\text{HCl}$  salt, m.  $171-2^\circ$  (decomposition), pyrolyzed by steam distillation with formation of a brown polymeric residue, even in the presence of a polymerization inhibitor such as hydroquinone, without isolation of the desired II. VI was similarly converted to the Mannich base but steam distillation failed to pyrolyze the base to the desired ketone III; in contrast to the behavior of the propiophenone analog (cf. Burckhalter and Fuson, CA 43, 1757c). The polymerization of I was accomplished.

188. Rausch, M. D., Vogel, M., and Rosenberg, H.,  
DERIVATIVES OF FERROCENE. PART III. THE PREPARATION OF SOME ACYLFERROCENES AND ALKYLFERROCENES, Charles J. Cleary Awards for Papers on Material Sciences, Washington, D. C., Library of Congress, Science and Technology Division, 1962, pp. 121-124 (N63-13243).

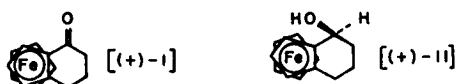
Refer to item No. 146 for abstract.

189. Schaaf, R. L. and Lenk, C. T.,  
FERROCENES.V. DIFUNCTIONAL FERROCENES FROM 1, 1'-FERROCENEDICARBOXYLIC ACID, Journal of Chemistry and Engineering Data, Vol. 9, No. 1, 1964, p. 103 (cf. CA 56, 14325g).

A series of 1, 1'-disubstituted ferrocenes was prepared from the corresponding diacid.

190. Schlogel, K. and Falk, H.,  
THE ABSOLUTE CONFIGURATION OF 1, 2-( $\alpha$ -OXOTETRAMETHYLENE) FERROCENE, Angewandte Chemie, Vol. 76, No. 13, 1964, p. 570.

The absolute configuration of the title compound (+)-isomer [(+)-I] was established by chemical means.



(+)-I  $[[\alpha]_D^{510} \text{ (EtOH)}]$  was reduced with  $\text{LiAlH}_4$  to a mixture of the epimeric endo- and exo-carbinols. Conversion into an acetate mixture with  $\text{Ac}_2\text{O}$  followed by stereoselective hydrolysis with aqueous  $\text{Me}_2\text{CO}$  gave the exo isomer [(+)-II]  $[[\alpha]_D^{113} \text{ (EtOH)}]$ . The reaction of (+)-II with racemic  $[\text{EtCHPhCO}]_2\text{O}$  gave (—)- $\text{EtCHPhCO}_2\text{H}$   $[[\alpha]_D -0.79^\circ \text{ (C}_6\text{H}_6)]$ . The asymmetrical C atom in (+)-II has S-configuration. Hence, the configuration of I is R.

191. Schlogel, K., Fried, M., and Falk, H.,  
FERROCENE DERIVATIVES. XX. FERROCENE ASYMMETRY,  
1. PREPARATION AND RESOLUTION OF ASYMMETRIC  
AMINES AND ALDEHYDES OF THE FERROCENE SERIES,  
XXI. 2. RELATIVE CONFIGURATIONS OF OPTICALLY  
ACTIVE  $\alpha$ -DISUBSTITUTED FERROCENE DERIVATIVES,  
*Monatshefte*, Vol. 95, No. 2, 1964, pp. 558-597 (cf. CA 59,  
3325g).

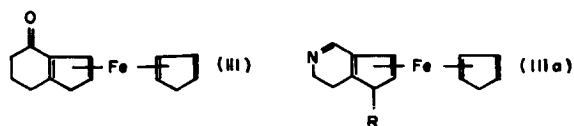
## XX

Conventional Grignard condensation of MeI with acetylferrocene gave 75 percent  $\text{C}_5\text{H}_5\text{FeC}_5\text{H}_4\text{CMe}_2\text{OH}$  (I), m.  $64-5^\circ$ . Reduction of I with  $\text{LiAlH}_4\text{-AlCl}_3$  in  $\text{Et}_2\text{O}$  gave 95 percent  $\text{C}_5\text{H}_5\text{FeC}_5\text{H}_4\text{Pr-iso}$ ,  $b_{0.03} 70-80^\circ$ .  $[\text{HOMe}_2\text{CC}_5\text{H}_4]_2\text{Fe}$  (II) was obtained in 83 percent yield by Grignard condensation of  $(\text{AcC}_5\text{H}_4)_2\text{Fe}$  with MeI in tetrahydrofuran (THF). Reduction of II with  $\text{LiAlH}_4\text{-AlCl}_3$  in THF gave 88 percent  $(\text{iso-PrC}_5\text{H}_4)_2\text{Fe}$  (III),  $b_{0.03} 95-100^\circ$ .  $\text{ClCONH}_2$ , prepared by pyrolysis of cyanuric acid in a stream of dry HCl, underwent an  $\text{AlCl}_3$ -catalyzed condensation with methylferrocene (IV) in  $\text{CH}_2\text{Cl}_2$  to give  $\text{MeC}_5\text{H}_4\text{FeC}_5\text{H}_4\text{CONH}_2$  (V), m.  $149-51^\circ$ , 1, 2-Me- $(\text{H}_2\text{NCO})\text{C}_5\text{H}_3\text{FeC}_5\text{H}_5$  (VI), and 1, 3-Me  $(\text{H}_2\text{NCO})\text{C}_5\text{H}_3\text{FeC}_5\text{H}_5$  (VII), m.  $120-6^\circ$ . V, VI, and VII were separated by chromatography on  $\text{Al}_2\text{O}_3$ .  $\text{iso-PrC}_5\text{H}_4\text{FeC}_5\text{H}_4\text{CONH}_2$  (VIII), m.  $111-14^\circ$ , [1, 2-(iso-Pr)  $(\text{H}_2\text{NCO})\text{C}_5\text{H}_3\text{FeC}_5\text{H}_5$  (IX), m.  $145-7^\circ$ , and [1, 3-(iso-Pr)  $(\text{H}_2\text{NCO})\text{C}_5\text{H}_3\text{FeC}_5\text{H}_5$  (X), m.  $174-8^\circ$ , were prepared and isolated in a similar fashion in yields of 35 percent, 12 percent, and 28 percent, respectively. Reaction between  $\text{HCONMePh}$ ,  $\text{POCl}_3$ , and IV in  $\text{CH}_2\text{Cl}_2$  gave a mixture of products from which a mixture of methylferrocenecarboxaldehydes was precipitated in the form of their semicarbazones. Regeneration of the free aldehyde mixture with 85 percent  $\text{H}_3\text{PO}_4$  followed by elution from an  $\text{Al}_2\text{O}_3$  column with 5:1  $\text{C}_6\text{H}_6\text{-Et}_2\text{O}$  gave only 1, 3-Me  $(\text{OHC})\text{C}_5\text{H}_3\text{FeC}_5\text{H}_5$  (XI), m.  $37-42^\circ$  (semicarbazone m.  $184-7^\circ$ ). XI could not be resolved.

$\text{iso-PrC}_5\text{H}_4\text{FeC}_5\text{H}_4\text{CHO}$  and 1, 3-Me (iso-Pr) $\text{C}_5\text{H}_3\text{FeC}_5\text{H}_5$  were prepared and separated in an analogous-manner. III was formylated with  $\text{HCONHMe}$  and  $\text{POCl}_3$  and the product purified via the semicarbazone to give 1, 3-(OHC) (iso-Pr)  $\text{C}_5\text{H}_3\text{FeC}_5\text{H}_5$ -H<sub>4</sub>Pr-iso (XII). XII was resolved by fractional crystallization of its (—)-menthydrazone (Woodward, et al., CA 35 1395<sup>8</sup>) to give 92 percent (+)-XII,  $[\alpha]_{\text{D}}^{22} 25 \pm 1^\circ$  (EtOH). Hydrolysis of V and VI with 15 percent KOH in BuOH gave 73 percent  $\text{MeC}_5\text{H}_4\text{FeC}_5\text{H}_4\text{CO}_2\text{H}$  (XIII), m. 148-50°, and 10 percent 1, 2-Me( $\text{HO}_2\text{C}$ ) $\text{C}_5\text{H}_3\text{FeC}_5\text{H}_5$  (XIV), m. 158-60°, respectively. Small amounts of the isopropylferrocenecarboxylic acids were obtained in similar fashion from VIII, IX, and X. XI and the Me esters of XIII and XIV were reduced with  $\text{LiAlH}_4$ - $\text{AlCl}_3$  to give 1, 3-Me<sub>2</sub> $\text{C}_5\text{H}_3\text{FeC}_5\text{H}_5$ , b<sub>0.1</sub> 50-60°, ( $\text{MeC}_5\text{H}_4$ )<sub>2</sub>Fe, m. 35-7°, and 1, 2-Me<sub>2</sub> $\text{C}_5\text{H}_3\text{FeC}_5\text{H}_5$ , m. 34-6°, respectively. VI was reduced with  $\text{LiAlH}_4$  in THF to give 90 percent 1, 2-Me( $\text{H}_2\text{NCH}_2$ ) $\text{C}_5\text{H}_3\text{FeC}_5\text{H}_5$  (XV), m. 20°. XV was resolved by fractional crystallization of its dibenzoyltartrate. Regeneration of the base from the insoluble fraction followed by precipitation with HCl gave 31 percent (+)-XV. HCl,  $[\alpha]_{\text{D}}^{16} 47.5 \pm 1.0^\circ$ . The mother liquor was evaporated in vacuo and the residue recrystallized from MeOH. The filtrate from the recrystallization was combined with (—)-malic acid in MeOH. The resulting salt was recrystallized twice from H<sub>2</sub>O and the free amine regenerated to give (—)-XV,  $[\alpha]_{\text{D}}^{18} -22 \pm 1^\circ$  (EtOH). Reduction of acetylferrocene oxime with  $\text{LiAlH}_4$  in THF gave a mixture of  $\text{EtNHC}_5\text{H}_4\text{FeC}_5\text{H}_5$ , m. 56-8°, and  $\text{MeCH}(\text{NHOH})\text{C}_5\text{H}_4\text{FeC}_5\text{H}_5$ , m. 158-9°, in yields of 32 and 45 percent, respectively. A similar reduction with H over Raney Ni in EtOH gave 32 percent  $\text{H}_2\text{NCHMeC}_5\text{H}_4\text{FeC}_5\text{H}_5$  (XVI), b<sub>0.05</sub> 90°. XVI was resolved by recrystallization of its salt with (+)-malic acid to give (+)-XVI. HCl,  $[\alpha]_{\text{D}}^{21} 2^\circ$  (EtOH), and (—)-XVI. HCl,  $[\alpha]_{\text{D}}^{20} -3 \pm 0.8^\circ$ .

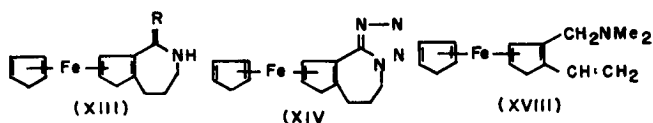
## XXI

A  $\text{C}_6\text{H}_6$  solution of  $\text{C}_5\text{H}_5\text{FeC}_5\text{H}_4(\text{CH}_2)_3\text{CO}_2\text{H}$  was converted into the acid chloride (I) with  $\text{PCl}_3$ . I underwent a Friedel Crafts cyclization with  $\text{AlCl}_3$  in  $\text{CH}_2\text{Cl}_2$  to give a mixture of 6.5 percent 1, 1'-( $\alpha$ -oxotetramethylene) ferrocene (II), m. 98-101°, and 42 percent III, m. 83-5°. III was resolved by repeated crystallization from EtOH of its (—)-menthyldrazone. Regeneration of the ketone from the least soluble



fraction gave (+)-III,  $[\alpha]_D^{25} 585 \pm 12^\circ$  (all in EtOH); (—)-III  $[\alpha]_D^{25} -300 \pm 7^\circ$ . A solution of N-formyl- $\beta$ -ferrocenylethylamine in absolute  $C_6H_6$  was refluxed with  $POCl_3$  to give 73 percent IIIa ( $R = H$ ),  $b_{0.001} 110-20^\circ$ . Hydrogenation of IV over Raney Ni in EtOH at  $50-60^\circ/100$  atm. for 2 days gave 84 percent the piperidine analog (V), m.  $88-9^\circ$ . A 40-50 percent yield was obtained by reduction with  $LiAlH_4$  in THF.  $C_5H_5FeC_5H_4CH_2CH_2N:CH_2$  (VI), m.  $101-3^\circ$ , was prepared in 80 percent yield from  $C_5H_5FeC_5H_4CH_2CH_2NH_2$  with 35 percent aqueous  $CH_2O$  in MeOH. VI underwent ring closure when treated with concentrated HCl in aqueous suspension to give 63 percent V.  $C_5H_5FeC_5H_4CH_2N:CH_2$  (VII), m.  $159-64^\circ$ , was prepared in 75 percent yield from the corresponding amine and aqueous  $CH_2O$ . An attempted ring closure of VII with concentrated HCl gave instead a yellow polymer (VIII). V was resolved by crystallization of its (—)-o, o'-dinitrodiphenic acid salt from hot MeOH. Regeneration of the amine from the insoluble fraction gave (+)-V,  $[\alpha]_D^{25} 30 \pm 2^\circ$ ; (—)-V,  $-32.4 \pm 1.5^\circ$ . d-III was quantitatively reduced to the isomeric alcohols, IX,  $b_{0.01} 110-20^\circ$ ,  $[\alpha]_D^{25} 39.2 \pm 2^\circ$ , and X, m.  $69-71^\circ$ ,  $[\alpha]_D^{25} 114 \pm 5^\circ$ , with  $LiAlH_4$  in  $Et_2O$ , in yields of 90 and 9 percent, respectively. Reaction of (+)-III with PhLi in  $Et_2O$  under N at room temperature gave 76 percent the  $\alpha$ -phenyl- $\alpha$ -hydroxy analog (Xa),  $b_{0.005} 125-35^\circ$ ,  $[\alpha]_D^{25} 190 \pm 6^\circ$ . A mixture of IX and X, obtained from optically pure (+)-III, was dehydrated by shaking for 2 hrs. at room temperature with a  $C_6H_6$  suspension of acidic  $Al_2O_3$ ; the product [(+)-XI], obtained in 75 percent yield, m.  $37-8^\circ$ ,  $[\alpha]_D^{25} -1920 \pm 15^\circ$ . (—)-XI was obtained in an analogous fashion from (—)-III. Analogous dehydration of (+)-Xa gave 90 percent the  $\alpha$ -Ph analog of (—)-XI,  $b_{0.001} 125-35^\circ$ ,  $[\alpha]_D^{25} -625 \pm 5^\circ$ . Dihydro derivative (XII) of XI, m.  $34-6^\circ$ , was obtained by reduction of III with  $LiAlH_4-AlCl_3$  in THF or by catalytic hydrogenation of XI over Pd-C in EtOAc. The  $\alpha$ -Ph derivative of XII,  $b_{0.001} 120-30^\circ$ ,  $[\alpha]_D^{25} 126 \pm 3^\circ$ , was similarly prepared in 75 percent yield by Na-EtOH reduction, as well as by  $LiAlH_4-AlCl_3$  reduction. A solution of (+)-III in  $CHCl_3$  was combined with a diluted  $C_6H_6$  solution of  $HN_3$

and the mixture was warmed to 40-50° with stirring while concentrated  $\text{H}_2\text{SO}_4$  was added dropwise. After  $\sim 1$  hr. the mixture was worked up to give a mixture of 27 percent XIII ( $\text{R} = \text{O}$ ) (XIIIa), m. 160-2° (petr. ether),  $[\alpha]_D -68 \pm 3^\circ$ ,  $-68 \pm 3^\circ$ , and 10-20 percent XIV, m. 122-3° (petr. ether),  $[\alpha]_D -81 \pm 3^\circ$ . Reduction of XIIIa with  $\text{LiAlH}_4$  in THF gave 60 percent XIII ( $\text{R} = \text{H}_2$ ) (XV), m. 54-7°,  $[\alpha]_D -9.5 \pm 0.5^\circ$  (EtOH),  $-34 \pm 1^\circ$  (cyclohexane). Shaking and refluxing a



$\text{CHCl}_3$  solution of XV with excess  $\text{MnO}_2$  gave a 22 percent yield of the dehydro compound (XVI),  $[\alpha]_D -270 \pm 15^\circ$ , homologous to IV. (—)-IV,  $[\alpha]_D = -1370 \pm 10^\circ$ , was similarly prepared by shaking a  $\text{CHCl}_3$  solution of (—)-V with  $\text{MnO}_2$ . The methiodide (XVII), m. 200° (decomposition), of the N-Me derivative of V was prepared by heating an MeOH solution of (—)-V with MeI and  $\text{Na}_2\text{CO}_3$  on a water bath. A solution of XVII in methanolic KOH was evaporated to dryness. Distillation of the residue and elution of the distillate from an  $\text{Al}_2\text{O}_3$  column with EtOAc gave 13.5 percent XVIII,  $b_{0.001} 100-20^\circ$ ,  $[\alpha]_D -107 \pm 2.5^\circ$ . Hydrogenation of XVIII in EtOH over Pd-C gave 91 percent 1, 2-Et( $\text{Me}_2\text{NCH}_2$ )- $\text{C}_5\text{H}_3\text{FeC}_5\text{H}_5$  (XIX),  $b_{0.001} 85-90^\circ$ ,  $[\alpha]_D 15 \pm 2^\circ$ . Quaternization of XIX with MeI and decomposition of the salt with methanolic NaOH gave 76 percent 1, 2-Et( $\text{HOCH}_2$ ) $\text{C}_5\text{H}_3\text{FeC}_5\text{H}_5$  (XX), m. 48-52°,  $[\alpha]_D -21.5 \pm 1^\circ$ . Shaking a  $\text{CHCl}_3$  solution of XX with  $\text{MnO}_2$  gave 53 percent 1, 2-Et( $\text{OHC}$ ) $\text{C}_5\text{H}_3\text{FeC}_5\text{H}_5$  (XXI),  $b_{0.01} 90-100^\circ$ ,  $[\alpha]_D 130 \pm 5^\circ$ . Aqueous hydrolysis of the MeMgI adduct of XXI in  $\text{Et}_2\text{O}$  gave 28 percent 1, 2-Et( $\text{H}_2\text{C}:\text{CH}$ ) $\text{C}_5\text{H}_3\text{FeC}_5\text{H}_5$  (XXII),  $b_{0.005} 70-5^\circ$ ,  $[\alpha]_D 660 \pm 17^\circ$ . Reduction of XXI with  $\text{LiAlH}_4$ - $\text{AlCl}_3$  in  $\text{Et}_2\text{O}$  gave 91 percent 1, 2-MeEt- $\text{C}_5\text{H}_3\text{FeC}_5\text{H}_5$  (XXIII),  $b_{0.02} 70-80^\circ$ ,  $[\alpha]_D -20.5 \pm 1.3^\circ$ . 1, 2-EtAc $\text{C}_5\text{H}_3\text{FeC}_5\text{H}_5$  (XXIV) was converted into its diastereoisomeric menthydrazone as described for III. After several recrystallizations from EtOH the free ketone was regenerated from the insoluble fraction to give (+)-XXIV,  $[\alpha]_{570} 25 \pm 5^\circ$ . Reduction of (+)-XXIV with  $\text{LiAlH}_4$  in  $\text{Et}_2\text{O}$  and dehydration of the resulting carbinol gave 54 percent XXII,  $[\alpha]_D 7 \pm 0.5^\circ$ . (+)-1, 2-Me( $\text{H}_2\text{NCH}_2$ ) $\text{C}_5\text{H}_3\text{FeC}_5\text{H}_5$  [(+)-XXV] was quaternized

with MeI and NaHCO<sub>3</sub> in MeCN. Treatment of the quaternary salt with concentrated NaOH gave 81 percent 1, 2-Me (HOCH<sub>2</sub>)-C<sub>5</sub>H<sub>3</sub>FeC<sub>5</sub>H<sub>5</sub> (XXVI), *b*<sub>0.01</sub> 75-85°, [*a*]<sub>D</sub> 5.9 ± 3°. Oxidation of XXVI with MnO<sub>2</sub> in CHCl<sub>3</sub> gave 93 percent 1, 2-Me (OHC)-C<sub>5</sub>H<sub>3</sub>FeC<sub>5</sub>H<sub>5</sub> (XXVII), *b*<sub>0.01</sub> 95-100°, [*a*]<sub>D</sub> 147 ± 8°. XXVII was reduced to a carbinol by hydrolysis of its MeMgI adduct. Dehydration of the carbinol with Al<sub>2</sub>O<sub>3</sub> gave a low yield of 1, 2-Me (H<sub>2</sub>C:CH)C<sub>5</sub>H<sub>3</sub>FeC<sub>5</sub>H<sub>5</sub> (XXVIII), *b*<sub>0.01</sub> 80-90°, [*a*]<sub>D</sub> ~660°. XXVIII polymerized readily and the optical rotation disappeared in a matter of min. Evaporation of an EtOH solution of XXVIII gave 1, 2-Me (EtOCHMe)C<sub>5</sub>H<sub>3</sub>FeC<sub>5</sub>H<sub>5</sub>, which was reduced to XXIII with LiAlH<sub>4</sub>-AlCl<sub>3</sub>. XXVII was converted into a carbinol with MeMgI. Reduction of the carbinol with an Et<sub>2</sub>O suspension of LiAlH<sub>4</sub>-AlCl<sub>3</sub> gave 65 percent (+)-XXIII, [*a*]<sub>D</sub> 12 ± 0.5°. Hydrogenation of XXVIII also gave small amounts of XXIII. (—)-XXV was quaternized with MeI and the salt was heated with aqueous KCN on a water bath to give 86 percent 1, 2-Me (NCCH<sub>2</sub>)C<sub>5</sub>H<sub>3</sub>FeC<sub>5</sub>H<sub>5</sub> (XXIX), *b*<sub>0.01</sub> 90-5°, [*a*]<sub>D</sub> -39 ± 2°. Reduction of XXIX with LiAlH<sub>4</sub> in THF gave 79 percent 1, 2-Me (H<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>)C<sub>5</sub>H<sub>3</sub>-FeC<sub>5</sub>H<sub>5</sub> (XXX), *b*<sub>0.05</sub> 75-80°, [*a*]<sub>D</sub> -9 ± 0.8°. Ring closure of XXX was carried out via the N-methylene derivative, which was prepared as described for V and VI. A 15 percent yield of the piperidine analog (XXXI) of IIIa (R = Me), *b*<sub>0.005</sub> 110-20°, [*a*]<sub>D</sub> ~20°, was obtained. Oxidation of XXXI with MnO<sub>2</sub> gave 20 percent IIIa (R = Me), *b*<sub>0.001</sub> 110-20°, [*a*]<sub>D</sub> 560 ± 7°.

192. Sugiyama, N. and Teitei, T.,  
 ABNORMAL REACTION OF FERROCENE WITH UNSATURATED DIBASIC ACID CHLORIDES AND NMR SPECTRA OF FERROCENE DERIVATIVES, Chemical Society of Japan Bulletin, Vol. 35, 1962, p. 1423.

Ferrocene reacts with fumaryl chloride in the presence of AlCl<sub>3</sub> in methylene chloride to give a mixture containing 1, 2-diferrocenoylthane. Similarly, citraconyl chloride yields 1, 2-diferrocenoylpropane and 1-methyl-2-ferrocenoylpropionic acid. The nuclear magnetic resonance spectral assignments are discussed.

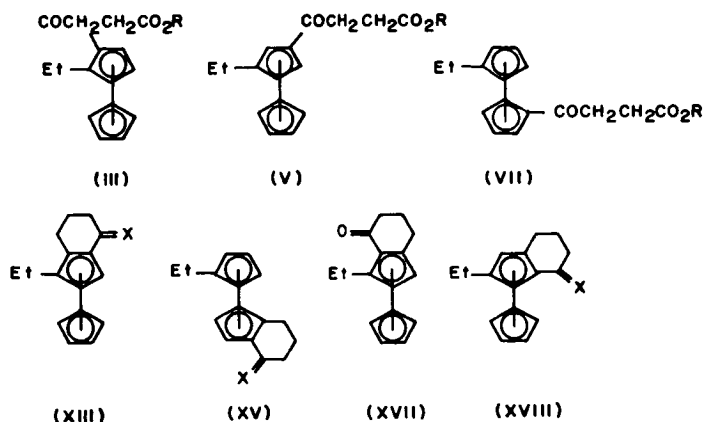
193. Sugiyama, N., Suzuki, H., Shioura, Y., and Teitei, T.,  
REACTION OF FERROCENE WITH ACYL CHLORIDES,  
Chemical Society of Japan Bulletin, Vol. 35, 1962,  
pp. 767-769.

A solution of ferrocene (0.054 mole, 10 g.) and  $\text{AlCl}_3$  (0.054 mole) in  $\text{CH}_2\text{Cl}_2$  combined with succinyl chloride (0.027 mole) in the same solvent was refluxed for 2 hrs. in a N atm., then poured on ice and the organic layer was separated into a neutral and an acidic fraction. From the acidic fraction was obtained  $\beta$ -ferrocenoylpropionic acid (I) (1.0 g.). The neutral fraction was dissolved in benzene, chromatographed on  $\text{Al}_2\text{O}_3$  and eluted: (1) with benzene, 3.3 g. ferrocene; (2) with benzene (second fraction),  $\gamma$ ,  $\gamma$ -diferrocenylbutyrolactone (II), m. 165.0-5.5° (EtOAc); (3) with EtOAc, 2.1 g. 1, 2-diferrocenoylethane (III), m. 185-6°, (EtOAc) [oxime m. 165-6° (decomposition) (methanol)]. The reduction of 1 g. III in anhydrous tetrahydrofuran with  $\text{LiAlH}_4$  in the same solvent yields 0.9 g. 1, 4-dihydroxy-1, 4-diferrocenylbutane (IV), m. 134-5° (ethanol). After the reduction of III as described above the tetrahydrofuran solution was shaken with 10 percent- $\text{H}_2\text{SO}_4$  and then with water, dried, and evaporated. The residue was dissolved in benzene and chromatographed on  $\text{Al}_2\text{O}_3$  to give quantitative 2, 5-diferrocenyltetrahydrofuran (V), m. 124.5-5.0°. V was also obtained by refluxing IV in  $\text{Ac}_2\text{O}$  for 1 hr. The reduction of 1 g. I with  $\text{NaBH}_4$  in ethanol yields 0.7 g.  $\gamma$ -ferrocenylbutyrolactone (VI), m. 130-1° (n-pentane). A solution of 0.054 mole phenacetyl chloride in  $\text{CH}_2\text{Cl}_2$  combined with 0.054 mole ferrocene and 0.054 mole  $\text{AlCl}_3$  in  $\text{CH}_2\text{Cl}_2$  was refluxed for 5 hrs. in a N atm., then poured on ice. The organic layer was washed, dried and evaporated and the residue was chromatographed on  $\text{Al}_2\text{O}_3$ . Elution with benzene and ethyl acetate yields 12.0 g. benzyl ferrocenyl ketone (VII), m. 128-9° (hexane); oxime m. 142-3° (decomposition) (methanol). The reduction of VII in anhydrous tetrahydrofuran with  $\text{LiAlH}_4$  in the same solvent yields quantitative 1-ferrocenyl-2-phenylethanol (VIII), m. 82.3° (pentane). VIII (1 g.) in anhydrous ether with  $\text{PCl}_5$  yields 0.7 g. 1-ferrocenyl-2-phenylethylene (IX), m. 121.0-1.5° (pentane). The ultraviolet spectra of II, IV, V, VI, and VIII (in 95 percent ethanol) are similar to those of ferrocene, the spectra of compounds III and VII correspond to those of acetylferrocene. IX has a maximum at 460 m $\mu$  ( $\epsilon$  1000). For infrared

spectra in KBr II-IX have bands at 1000 and 1110  $\text{cm.}^{-1}$ , II and VI at 1770, 1780; III and VII at 1660, 1665; IV and VIII at 3400, 3480; IX at 1640, 960  $\text{cm.}^{-1}$ .

194. Tainturier, G. and Tirouflet, J.,  
 METALLOCENES. VI. GENERAL METHOD FOR THE  
 IDENTIFICATION OF 1, 2-, 1, 3-, AND 1, 1'-DISUBSTITUTED FERROCENES, SYNTHESIS OF FOUR 1, 2-( $\alpha$ -OXOTETRAMETHYLENE) ETHYLFERROCENES, Société Chimique de France Bulletin, No. 2, 1966, pp. 595-600 (in French) (cf. CA 62, 16294c).

Ethylferrocene (I) and  $\text{MeO}_2\text{CCH}_2\text{CH}_2\text{COCl}$  (II) (equimolar amounts) in the presence of  $\text{AlCl}_3$  yielded a mixture of III (R = Me) (IV), V (R = Me) (VI), and VII (R = Me) (VIII). III, V, and VII (all with R = H) were reduced to the corresponding 4-(ethylferrocenyl) butyric acids which were cyclized. Acetylferrocene (IX) (45.6 g.) reduced with 450 g. Zn-Hg in 450 cc. 10N HCl yielded 34 g. I,  $b_p$  110-12°. I (17.5 g.) in 100 cc. dry  $\text{CH}_2\text{Cl}_2$  treated dropwise with stirring during about 45 min. with 11 g.  $\text{AlCl}_3$  in 200 cc.  $\text{CH}_2\text{Cl}_2$  containing 12.3 g. II and stirred 2 hrs. at room temperature, and the resulting crude, dark red, oily product (23 g.) chromatographed on  $\text{Al}_2\text{O}_3$  yielded 3.75 g. unreacted I, 2.1 g. IV, m. 50-2° (pentane),  $R_f$  0.76 (5:4 petroleum ether-Et<sub>2</sub>O,  $\text{SiO}_2$ ), 1.8 g. VIII, red oil,  $R_f$  0.57, and 0.4 g. VI, red oil,  $R_f$  0.53. The appropriate ester treated 0.5 hr. at room temperature with two equivalents KOH in EtOH yielded III (R = H), m. 120° (hexane), VII (R = H), m. 94-6° (hexane), and V (R = H), m. 108-10° (hexane), respectively. The appropriate acid (3 g.) in 40 cc. AcOH and 10 cc.  $\text{H}_2\text{O}$  refluxed 4 hrs. with 30 g. amalgamated Zn and 3 g.  $\text{HgCl}_2$  in 25 cc. concentrated HCl while being treated with an

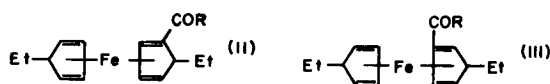




additional 10 cc. concentrated HCl in portions yielded 4-(2-ethylferrocenyl) butyric acid (X), m. 68-9° (pentane), 4-(1'-ethylferrocenyl) butyric acid (XI), m. 45-6° (pentane), and 4-(3-ethylferrocenyl) butyric acid (XII), oil, respectively. X (1.6 g.) in 16 cc. dry CH<sub>2</sub>Cl<sub>2</sub> added dropwise at room temperature under N to 1.460 g. (CF<sub>3</sub>CO)<sub>2</sub>O in 6 cc. CH<sub>2</sub>Cl<sub>2</sub>, refluxed 15 min., and worked up yielded 0.80 g. XIII (X = O) (XIV), m. 48° (pentane), R<sub>f</sub> 0.47 (5:1 C<sub>6</sub>H<sub>6</sub>Et<sub>2</sub>O, SiO<sub>2</sub>). XI (1 g.) and 0.91 g. (CF<sub>3</sub>CO)<sub>2</sub>O gave similarly 0.88 g. XV (X = O) (XVI), m. 67° (pentane), R<sub>f</sub> 0.53. XII (0.30 g.) and 0.27 g. (CF<sub>3</sub>CO)<sub>2</sub>O gave similarly 0.18 g. red oil which chromatographed on 100 g. Al<sub>2</sub>O<sub>3</sub> yielded 0.033 g. XVII, m. 58-60°, R<sub>f</sub> 0.72, and 0.020 g. XVIII (R = O) (XIX), m. 67°, R<sub>f</sub> 0.48. VI-VIII mixture saponified, the crude acid mixture reduced with Hg-Zn and HCl, and the product (12.14 g.) treated with 11.03 g. (CF<sub>3</sub>CO)<sub>2</sub>O yielded after 9 successive chromatographies on Al<sub>2</sub>O<sub>3</sub> 1.61 g. XVII, m. 58°, 3.80 g. XVI, m. 67°, and 0.95 g. XIX, m. 66-7°. XIV (2.34 g.) subjected to a Clemmensen reduction gave 1.34 g. XIII (X = H<sub>2</sub>) (XX), b<sub>2</sub> 134-6°. XVII (3.1 g.) gave similarly 1.5 g. XX. XIX gave 0.73 g. XVIII (X = H<sub>2</sub>), b<sub>2</sub> 137-8°, and XVI (3.1 g.) yielded 1.5 g. XV (X = H<sub>2</sub>), b<sub>2</sub> 137-9°. II (7.5 g.) added with stirring and cooling to 26.6 g. AlCl<sub>3</sub> in 200 cc. dry CH<sub>2</sub>Cl<sub>2</sub>, treated with 11.4 g. IX in 100 cc. dry CH<sub>2</sub>Cl<sub>2</sub>, and stirred 2 hrs. at room temperature gave 8.9 g. red Me ester (XXI) of 3-(1'-acetylferrocenyl) propionic acid (XXII), m. 71-2° (hexane). XXI (15.4 g.) and 5.04 g. KOH in 150 cc. EtOH kept 45 min at room temperature yielded 9.8 g. XXII, m. 182° (AcOH). XXII (9 g.) in 100 cc. AcOH subjected to a Clemmensen reduction yielded 4.7 g. XI, m. 45-6° (pentane).

195. Tainturier, G. and Tirouflet, J.,  
STRUCTURE OF TRISUBSTITUTED ISOMERS OBTAINED  
FROM 1, 1'-DIETHYLFERROCENE, Comptes Rendus, Vol.  
258, No. 23, 1964, pp. 5666-5668.

Acylation of 1, 1'-diethylferrocene (I) gives II (R = H), b<sub>2</sub> 151-2°, and II (R = Me), b<sub>3</sub> 150°, and III (R = H), b<sub>2</sub> 142°, and III (R = Me), b<sub>3</sub> 152°, in 3:7 ratio, respectively. II and III may be separated by gas



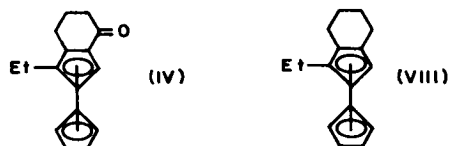
chromatography. Various derivatives were prepared and their structures determined (R, melting point, and boiling point given): II:  $\text{CH}_2\text{CH}_2\text{NMe}_3\text{I}$ ,  $162^\circ$  (decomposition), -;  $\text{CH}_2\text{CH}_2\text{CN}$ , -,  $b_3$   $214^\circ$ ;  $\text{CO}_2\text{H}$ ,  $54^\circ$ , -; III:  $\text{CH}_2\text{CH}_2\text{NMe}_3\text{I}$ , -, -;  $\text{CH}_2\text{CH}_2\text{CN}$ , -,  $b_3$   $210^\circ$ ;  $\text{CO}_2\text{H}$ ,  $52^\circ$ , -. There were no interconversions in these reactions.

196. Teunissen, H. P.,  
DIACYL FERROCENES, Netherlands Patent 96,227, 15  
December 1960, U. S. Applied 2 November 1953, 3 pp.

Diacylferrocenes are prepared by the reaction of ferrocene with an acid halide or an acid anhydride in the presence of an acidic catalyst, e. g.  $\text{AlCl}_3$ , and an organic solvent, such as  $\text{CH}_2\text{Cl}_2$ . The complex of the diacylferrocene, formed by the reaction, and the catalyst is easily soluble in  $\text{CH}_2\text{Cl}_2$ , which simplifies the process, giving a high yield, e. g., 150 parts  $\text{CH}_2\text{Cl}_2$ , 16 parts anhydrous  $\text{AlCl}_3$ , and 9.4 parts  $\text{AcCl}$  are mixed, heated to boiling, and 10 parts ferrocene added in  $\frac{1}{2}$  hr. Cooling, pouring on ice water, and extracting with  $\text{CH}_2\text{Cl}_2$  gives the diacetylferrocene in 9.14-g. yield after recrystallization from EtOH-heptane and water. From the mother liquor another 1.4 g. is obtained.

197. Tirouflet, J. and Tainturier, G.,  
GENERAL METHOD FOR IDENTIFICATION OF DISUBSTITUTED FERROCENE DERIVATIVES. SYNTHESIS AND STRUCTURE OF THE FOUR 1, 2-( $\alpha$ -OXOTETRAMETHYLENE) FERROCENES, Tetrahedron Letters, No. 47, 1965, pp. 4177-4179 (In French) (cf. CA 59, 1678d).

Treatment of ethylferrocene with  $\text{MeO}_2\text{CCH}_2\text{CH}_2\text{COCl}$  under monosubstitution conditions, chromatographic separation of the Me esters, and sapon. gave the  $3\beta$ -(ethylferrocenoyl)-propionic acids, m.  $120^\circ$ ,  $108-10^\circ$ ,  $94-6^\circ$ , reduced according to Clemmensen to the corresponding  $\delta$ -(ethylferrocenyl)-butyric acids (I, II, III), m.  $68^\circ$ , oil,  $45-6^\circ$ . I and III were cyclized with  $(\text{CF}_3\text{CO})_2\text{O}$  to 1, 2-( $\alpha$ -oxotetramethylene)-3-ethylferrocene (IV), m.  $48^\circ$ , and 1, 2-( $\alpha$ -oxotetramethylene)-1'-ethylferrocene (V), m.  $67^\circ$ . On the contrary, cyclization of II and separation of the product by chromatography gave



1, 2-( $\alpha$ -oxotetramethylene)-5-ethylferrocene (VI), m. 58-60°, and 1, 2-( $\alpha$ -oxotetramethylene)-4-ethylferrocene (VII), m. 66-7°. Clemmensen reduction converted both IV and VI to the same hydrocarbon, 1, 2-tetramethylene-3-ethylferrocene (VIII),  $b_2$  134-6°. V gave 1, 2-tetramethylene-1'-ethylferrocene,  $b_2$  137-9°, and VII was reduced to 1, 2-tetramethylene-4-ethylferrocene,  $b_2$  137-8°. The spectroscopic identification of the hydrocarbons VIII sufficed to demonstrate the structure of all the mentioned compounds. The method is not limited to succinoyl derivatives.

198. Tirouflet, J., Monin, J. P., Tainturier, G., Dabard, R., Thomson, Rosenblum, et al.,  
HOMO AND HETERO RING ISOMER PROBLEMS OF THE FERROCENE SERIES, Comptes Rendus, Vol. 256, 1963, pp. 433-435 (In French) (cf. CA 54, 3360c and CA 57, 15149b).

Cyclization of ferrocene 1, 1'-dibutanoic acid leads to 2 isomeric cyclanones, m. 160° and 170°, which differ in the direction of their rotation during the reaction. Succinylation of ethylferrocene and of 1, 1'-diethylferrocene give, respectively, the 3 (m. 120°, 94-6°, 106-8°) or 2 (m. 54°, 52°) isomers foreseen for the sandwich structure.

199. Toma, S.,  
DERIVATIVES OF FERROCENE. XII. FERROCENE ANALOGS OF CHALCONES, Chemické Zvesti, Vol. 19, No. 9, 1965, pp. 703-710 (In Slovak) (cf. CA 63, 7041d).

By the aldol condensation of the acetylferrocenes or 1-acetyl-1'-benzoylferrocenes with aromatic aldehydes, ferrocene analogs of chalcones were prepared and determined by thin-layer chromatography and polarography. In the chalcones derived from the acetylferrocenes the halfwave potentials were plotted in the diagram against Hammett's  $\sigma$  constant. A linear relationship was determined as expressed in the equation:  $\Delta E_{1/2}^0 = +0.17 \sigma$ . In the chalcones

derived from the 1-acetyl-1'-benzoylferrocenes, the values of halfwave potentials practically do not depend on the nature of the substituent. Analyses of 22 prepared compounds are given.

200. Westman, L. and Rinehart, K. L., Jr.,  
OPTICALLY ACTIVE FERROCENECARBOXYLIC ACID,  
Acta Chemica Scandinavica, Vol. 16, 1962, pp. 1199-1205.

1, 1'-Dimethylferrocene-(±)-2-carboxylic acid, m. 123-6°, and its (±)-3-isomer (I), m. 108-9.5°, are separated by chromatography of their p-BrC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub> esters over Al<sub>2</sub>O<sub>3</sub>. I was resolved by its cinchonidine salt, m. 169-71°, which gives the (+)-acid, m. 119-21°,  $[\alpha]_D^{22}$  37.5 ± 1.5° (c 0.8, CHCl<sub>3</sub>), and by its quinidine salt, m. 118-23°, which gives the (—)-acid, m. 119-21°,  $[\alpha]_D^{22}$  -36.0 ± 1.0°, the first reported resolution of a trisubstituted ferrocene. The mixture of acids, readily separated into mono- and dicarboxylic acids based on their Et<sub>2</sub>O soly., was prepared by treating 1, 1'-dimethylferrocene with BuLi and then CO<sub>2</sub>.

201. Wolf, L. and Henning, H.,  
FERROCENE-SUBSTITUTED 1, 3-DIKETONES, Zeitschrift fuer Chemie, Vol. 3, No. 12, 1963, pp. 469-470 (cf. CA 52, 10065d).

Some ferrocenoyl compounds of the type (C<sub>5</sub>H<sub>5</sub>)Fe(C<sub>5</sub>H<sub>4</sub>-COCH<sub>2</sub>R) (I) were prepared for a study of their complex chemical behavior. Ferrocene was treated with Ac<sub>2</sub>O in the presence of 70 percent H<sub>3</sub>PO<sub>4</sub> to give acetylferrocene (II) which oxidized with iodine in C<sub>5</sub>H<sub>5</sub>N gave ferrocenemono-carboxylic acid; the latter with CH<sub>2</sub>N<sub>2</sub> gave the Me ester (III). Condensation of III with II in the presence of NH<sub>2</sub>Na gave diferrocenoylmethane (IV), dark brick-red needles, m. 162.5-3.5°; in concentrated mineral acids IV dissolved with deep violet color; with FeCl<sub>3</sub> IV gave a dark green color; IV and (NH<sub>2</sub>)<sub>2</sub> gave 3, 5-diferrocenylpyrazole, ochre crystals, decomposing 300°. Similarly, the following I were prepared: ferrocenoyl-2-furoylmethane (V), dark red crystals, m. 88° [with (NH<sub>2</sub>)<sub>2</sub> it gave 3-ferrocenyl-5-(2-furyl)-pyrazole, orange red, m. 244°]; ferrocenoyl-2-thenoylmethane (VI), dark red, m. about 110°, ferrocenoyl-picolinoylmethane (VII), C<sub>18</sub>H<sub>15</sub>O<sub>2</sub>NFe, dark purple needles,

m. 136.5-7.5° [with (NH<sub>2</sub>)<sub>2</sub> it gave 3-ferrocenyl-5-picolinylpyrazole, golden yellow leaflets, m. 223°]; ferrocenoylnicotinoylmethane (VIII), wine red crystals, m. 127.5-8.5° [with (NH<sub>2</sub>)<sub>2</sub>, it gave 3-ferrocenyl-5-nicotinyopyrazole, orange crystals, m. 275°]; ferrocenoylisonicotinoylmethane (IX), dark red crystals, m. 164-5° [with (NH<sub>2</sub>)<sub>2</sub> it gave 3-ferrocenylisonicotinylpyrazole, orange crystals, m. 225°]. With FeCl V and VI gave a dark red color, VII, VIII, and IX a red color changing to deep green. VII, VIII, and IX gave characteristic colors with mineral acids. All I were insoluble in H<sub>2</sub>O, but soluble in organic solvents. VII and MeI at 100° gave a methiodide, C<sub>19</sub>H<sub>18</sub>O<sub>2</sub>NFeI, a blue compound I gave very readily complex compounds of which a Cu and Th derivative has been prepared. VII-IX gave a new type of complex compounds since, because of the heterocyclic N, they can react as a monodentate ligand and also as a diketone chelate former.

202. Wyandotte Chemical Corporation, Wyandotte, Michigan, and University of Illinois, Urbana, Illinois,  
SYNTHESIS OF METAL-CYCLOPENTADIENYL DERIVATIVES  
FOR USE AS ULTRAVIOLET ABSORBERS by R. L. Schaaf  
and K. L. Rinehart, Jr., May 1961, Report No. WADD-TR-61-108 AD-268 773, Contract No. AF 33(616)-7214,  
Project 7312, Task 73120 (Unclassified Report).

In a search for ferrocene derivatives that may be useful as protective ultraviolet absorbers, 12 candidate ferrocenes were synthesized, the spectral characteristics in the 2000 to 5000 Å region were obtained, and the melting points, microboiling points, and solubility properties of the ferrocenes were determined. Thus, 2-methoxybenzoylferrocene, 2, 4-dimethoxybenzoylferrocene, benzoylferrocene, 1, 1'-dibenzoylferrocene, and diferrocenyl ketone were prepared by Friedel-Crafts reactions on ferrocene. The methoxy compounds were converted to 2-hydroxybenzoylferrocene, 2, 4-dihydroxybenzoylferrocene, and 2-hydroxy-4-methoxybenzoylferrocene by treatment with aluminum chloride. Ethyl ferrocenemonocarboxylate and diethyl 1, 1'-ferrocenedicarboxylate were prepared from the crude acids, and basic hydrolyses of these esters furnished pure ferrocenemonocarboxylic acid and 1-carboxy-1'-carbethoxyferrocene. At 345°C, ferrocenemonocarboxylic acid decomposed to pure ferrous ferrocenemonocarboxylate.

Studies have been continued of the preparation of substituted ferrocenes, particularly those containing oxygenated and nitrogenated groups. The 1, 1'-dimethylferrocenedicarboxylic acids have been prepared and partially separated. Nitroferrocene, 1, 1'-dinitroferrocene, azoferrocene, azoxyferrocene, and aminoferrocene have been prepared and their properties determined.

#### D. Aryl Ferrocenes

203. Beckwith, A. L. J. and Leydon, R. J.,  
FREE-RADICAL PHENYLATION OF FERRICENIUM  
ION, American Chemical Society Journal, Vol. 86, 1964,  
p. 972.

When ferricenium borofluoride (0.011 mole) and phenylazotriphenylmethane (0.011 mole) in acetic acid were maintained at 75° for 1.5 hrs. nitrogen was evolved and the characteristic color of the ferricenium ion faded. The products isolated were phenylferrocene (0.002 mole) and triphenylcarbinol (0.006 mole) together with small amounts of trityl ferrocene, triphenylmethane, and tetraphenylmethane. Some ferrocene was recovered. It has been previously demonstrated that phenylazotriphenylmethane is without effect on neutral ferrocene. There is little doubt that this represents an authentic example of free radical phenylation of ferricenium ion.

204. Beckwith, A. L. J. and Leydon, R. J.,  
FREE-RADICAL SUBSTITUTION OF FERRICINIUM ION  
THE MECHANISM OF THE ARYLATION OF FERROCENE,  
Tetrahedron, Vol. 20, 1964, pp. 791-801.

Formation of ferricinium ion is the primary step in reactions of ferrocene with t-butyl perbenzoate, benzoyl peroxide, and N-nitrosoacetanilide. Ferrocene is unaffected by treatment with free-radical reagents or arenediazonium salts under experimental conditions precluding formation of ferricinium ion. 1-Cyano-1-methylethyl radicals and benzyl radicals each react with ferricinium ion forming appropriately substituted ferrocenes. Experimental evidence supports the view that arylation of ferrocene with arenediazonium salts proceeds by attack of free aryl radicals on ferricinium ion.

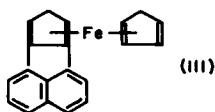
It is suggested that the relative ease of reaction of a substituted ferricinium ion with free radicals may be correlated with its reduction potential.

205. Brandeis University, Waltham, Massachusetts,  
INTRAANNULAR RESONANCE EFFECTS IN FERROCENE  
by M. Rosenblum, June 1961, Report No. AROD-2258-1,  
AD-265 593, Contract No. A19 0200 RD 4757.

A tabular summary is presented for the synthesis of the arylferrocenes, the acetylation studies of mono- and diarylferrocenes along with the results of competition experiments, and the ultraviolet absorption spectral data for these compounds.

206. Little, W. F., Nielsen, B., and Williams, R.,  
BISARYLATION OF FERROCENE, Chemistry and Industry  
(London) No. 5, 1964, pp. 195-197.

Diazotization of m-phenylenediamine in 50 percent  $\text{HBF}_4$  gives an immediate precipitate of a stable bisdiazonium fluoroborate (I). As the dry salt, I was used to arylate ferrocene in  $\text{CH}_2\text{Cl}_2$  to give 16 percent m-diferrocenylbenzene (II), m.  $189-91^\circ$ , and some phenylferrocene. Similarly,



benzidine gave 7 percent p, p'-diferrocenylbiphenyl, m.  $> 300^\circ$  (decomposition), and 13 percent p-biphenylferrocene, m.  $165-6.5^\circ$ . Of the three possible products from 1, 8-diaminonaphthalene only 1, 2-perinaphthaleneferrocene (III), m.  $158-60^\circ$ , has been isolated. The nuclear magnetic resonance and ultraviolet spectra of I, II, and III are discussed.

207. McVey, S. and Pauson, P. L.,  
FERROCENE DERIVATIVES. XIV. POLYARYLCYCLO-  
PENTADIENYLIRON COMPOUNDS, Chemical Society  
Journal, August 1965, pp. 4312-4318 (cf. CA 58, 13988d).

Reactions of polyarylcyclopentadienes with iron carbonyl or their anions with ferrous chloride have given a range of highly substituted ferrocenes and cyclopentadienyliron carbonyls. Bromopenta-(or tetra-) phenylcyclopentadiene reacts with pentacarbonyliron to give dicarbonylbromopenta-(or tetra-) phenylcyclopentadienyliron.

208. Nesmeyanova, A. N., Perevalova, E. G., and Beinoravichute, Z. A.,  
REDUCTION OF FERROCENECARBOXYLIC ACIDS,  
Doklady Akademii Nauk SSSR, Vol. 112, 1957, pp. 439-440.

Refer to item No. 177 for abstract.

209. Nesmeyanova, A. N., Sazonova, V. A., and Drozd, V. N.,  
INTRODUCTION OF AROMATIC AND HETEROCYCLIC  
RADICALS INTO FERROCENE. REACTION OF BROMO-  
FERROCENE WITH ORGANOMAGNESIUM COMPOUNDS,  
(Foreign title not available), Translated into English from  
the Russian by R. C. Taylor, U. S. Army Missile Command,  
Redstone Arsenal, Alabama, RSIC-573, June 1966 (Doklady  
Akademii Nauk SSSR, Vol. 165, No. 3, 1965, pp. 575-577  
(In Russian)).

PhMgBr in Et<sub>2</sub>O treated with bromoferrocene in the presence of Cu<sub>2</sub>Br<sub>2</sub> and powered Cu under N, then heated finally to 130° (after removal of Et<sub>2</sub>O) 40 min. gave after an aqueous treatment 75-81 percent phenylferrocene, m. 110-11°. Similarly was prepared 87 percent 2-thienylferrocene, m. 116.5-17.5°; 73 percent 1-naphthylferrocene, m. 93.5-4.5°. Pyrrolylmagnesium bromide and bromoferrocene treated as above gave 15 percent 2-pyrrolylferrocene, m. 148-9.5°, and 11 percent 3-pyrrolylferrocene, m. 188-8.5°, which were separated on Al<sub>2</sub>O<sub>3</sub> by successive elution with heptanebenzene. Similarly indolylmagnesium bromide gave 11 percent 3-indolylferrocene, m. 133-4.5°, along with some diferrocenyl and 14-16 percent N-indolylferrocene, m. 89-90°. C<sub>6</sub>H<sub>11</sub>MgCl in this reaction gave 80 percent ferrocene and cyclohexene.

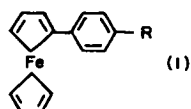


210. Shih, S., Sung, H., and Li, F.,  
TRANSLATIONS ON COMMUNIST CHINA'S SCIENCE AND  
TECHNOLOGY° NO. 156, SYNTHESIS AND CERTAIN  
REACTIONS OF P.TOLYLFERROCENE (Foreign title not  
available), Translated into English from Chinese by Joint  
Publications Research Service, Washington, D. C., N65-  
20518, 9 March 1965, pp. 33-35 (K'o Hsueh T'ung Pao  
(Peiping)), No. 1, 17 January 1965, pp. 78-79.

Bloody-red rhombohedral crystals of paratolylferrocene were synthesized by arylation of the diazonium salt of paraamino benzaldehyde with ferrocene. A binary substituted compound of diparatolylferrocene, in bloody-red needles, was also obtained. Reactions in various solvents were studied, and constants of melting and decomposition temperature determined.

211. Shih, S., Sung, H., and Li, F.,  
SYNTHESIS AND REACTIONS OF p-FORMYLPHENYL-  
FERROCENE, K'o Hsueh Tung Pao No. 1, 1965, pp. 78-79  
(In Chinese).

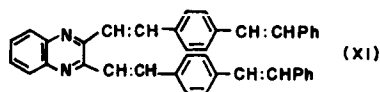
p-(Formylphenyl) ferrocene (I) ( $R = \text{CHO}$ ) (Ia), with bis (p-formylphenyl) ferrocene (II) as a byproduct was prepared by treating ferrocene with  $4\text{-OHCC}_6\text{H}_4\text{N}_2\text{HSO}_4$ . I ( $R = \text{CH}_2\text{OH}$ ) (III) and I ( $R = \text{CO}_2\text{H}$ ) (IV) were formed when Ia was heated in a NaOH-EtOH solution. Ia condensed readily



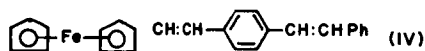
with malonic acid and with  $\text{PhCOMe}$  to form I ( $R = \text{CH:CHCO}_2\text{H}$ ) (V) and I ( $R = \text{CH:CHBz}$ ) (VI), respectively. Ia was treated with  $\text{MeMgI}$  followed by hydrolysis to form I [ $R = \text{CH(OH)Me}$ ] (VII). The color and melting point of the compounds are: I, red,  $136.5\text{--}37^\circ$ ; II, red  $229.5\text{--}30^\circ$ ; III, golden yellow,  $111.5\text{--}12^\circ$ ; IV, golden yellow,  $240\text{--}6^\circ$ ; V, reddish orange,  $224\text{--}5.5^\circ$ ; VI, golden yellow,  $128.5\text{--}9.5^\circ$ ; VII, golden yellow,  $104.5\text{--}5.0^\circ$ .

## E. Olefinic and Alkynyl Ferrocene Derivatives

212. Drefahl, G., Ploetner, G., and Winnefeld, I.,  
 ARYLETHYLENE DERIVATIVES OF FERROCENE, Berichte,  
 Vol. 95, 1962, pp. 2788-2791.



The preparation and properties of arylethylene derivatives of ferrocene were described. Ferrocenecarboxaldehyde (I) (1 g.) in 30 cc. absolute EtOH treated with an equivalent amount 0.2M LiOEt in EtOH and the mixture diluted with H<sub>2</sub>O and refrigerated yielded 45 percent styrylferrocene, m. 118° (MeOH). I (1 g.) and 2.5 g. [p-MeC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>PPh<sub>3</sub>] Cl with 30 cc. 0.2M LiOEt-EtOH gave 53 percent p-methylstyrylferrocene, m. 131° (MeOH). 9-Anthrylmethyltriphenylphosphonium chloride (3 g.) in 20 cc. absolute EtOH treated with 1 g. I in 20 cc. absolute EtOH and 28 cc. 0.2M LiOEt-EtOH and cooled yielded 23 percent 1-(9-anthryl)-2-ferrocenylethylene (II), m. 168° (absolute EtOH). [PhCH:CHCH<sub>2</sub>PPh<sub>3</sub>] Cl (3 g.) and 1 g. I in 50 cc. absolute EtOH with one equivalent LiOEt-EtOH yielded 35 percent 1-phenyl-4-ferrocenylbutadiene (III), m. 192° (hexane). [p-PhCH:CHC<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>PPh<sub>3</sub>] Br (3 g.) in 50 cc. absolute EtOH treated with 1 g. I in 20 cc. EtOH and an equivalent amount 0.2M LiOEt-EtOH yielded 33 percent 1-(p-stilbenyl)-2-ferrocenylethylene (IV), m. 220°. I (1 g.) and 3 g. [p-C<sub>6</sub>H(CH<sub>2</sub>PPh)<sub>2</sub>] Cl<sub>2</sub> treated with 50 cc. 0.2M LiOEt-EtOH and refrigerated gave 31 percent 1, 4-bis (2-ferrocenylvinyl) benzene, m. 141-2° (absolute EtOH). The ultraviolet absorption spectra of 1-(9-anthryl)-2-phenylethylene, II, (PhCH:CH)<sub>2</sub>, and III are recorded.



213. Egger, H. and Schlogel, K.,  
FERROCENE DERIVATIVES. XXIII. FERROCENYLACETYLENES. 4. PREPARATION AND LIGHT-ABSORPTION OF FERROCENYLTHIOPHENES AND FERROCENYLACETYLENES, Monatshefte fuer Chemie, Vol. 95, No. 6, 1964, pp. 1750-1758 (In German) (cf. CA 59, 7557f; CA 61, 14708h, and CA 61, 16091g).

A solution of 0.24 g. Na in 20 ml. EtOH was saturated at room temperature with  $H_2S$ , 0.62 g. ferrocenylphenylbutadiene added, and the mixture refluxed for 3 hrs. and worked up to yield 51 percent 2-ferrocenyl-5-phenylthiophene (I), m.  $142-3^\circ$  (petr. ether). 2-Ferrocenyl-5-hydroxymethyl thiophene (II), m.  $115-117^\circ$ , was similarly prepared (70 percent) from 5-ferrocenyl-2, 4-pentadien-1-ol (III). III, m.  $87-90^\circ$ , was prepared (45 percent) by refluxing 0.14 g. ferrocenylacetylene (IV) and 0.2 g. propargyl alcohol in a mixture of 10 ml.  $Et_2O$ , 5 ml. MeOH, and 10 ml.  $C_5H_5N$  with 0.8 g.  $Cu(OAc)_2$  2.5 hrs. 2, 5-Diferrocenylthiophene (V), m.  $208-10^\circ$  (cyclohexane), was prepared (80 percent by heating 1, 4-ferrocenyldiacetylene (VI) BuOH, and  $H_2S$  2.5 hrs. 2-Ferrocenyl-5-formylthiophene (VII) was prepared by shaking a  $CHCl_3$  solution of II with  $\sim 10$  parts active  $MnO_2$  several hrs., m.  $103-4^\circ$  (petr. ether). 2-Ferrocenyl-5-methylthiophene (VIII) was prepared by refluxing 0.3 g. II in 5 ml. absolute tetrahydrofuran (THF) with 80 mg.  $LiAlH_4$  and 270 mg.  $AlCl_3$  1 hr., m.  $72-4^\circ$ . 4-Ferrocenylbenzaldehyde (IX) was prepared from 24 g. o-aminobenzaldehyde by diazotizing its solution in 220 ml. cold 10 percent  $H_2SO_4$  with 13.8 g.  $NaNO_2$  in 60 ml.  $H_2O$ . After 15 min. 5 g. urea was added, 9.3 g. ferrocene in 350 ml. AcOH added, and the mixture kept 18 hrs. and worked up to give 6 percent IX, m.  $121-5^\circ$  (petr. ether, aqueous MeOH); semicarbazone m.  $200-5^\circ$  (decomposition) (MeOH- $H_2O$ ). Triphenylphosphine carbethoxymethylene (2 g.) in 10 ml.  $C_6H_6$  was added dropwise to a solution of the  $COCl$  derivative of ferrocene in 10 ml.  $C_6H_6$ , and the mixture warmed slightly 1 hr. to prevent crystallization and worked up to give 1.3 g. product, which was pyrolyzed at  $220-50^\circ/0.2$  mm. to give Et ferrocenylpropionate (X), m.  $96-7^\circ$  (petr. ether). A solution of 0.31 g. V in 10 ml. absolute  $Et_2O$  was stirred with 80 mg.  $LiAlH_4$  10 min. at

-10° and worked up, the crude carbinol in 10 ml.  $\text{CH}_2\text{Cl}_2$  shaken 18 hrs. with 2 g. active  $\text{MnO}_2$ , and the mixture worked up to give 50 percent 3-ferrocenylpropynal (XI), m. 78-9° (petr. ether). Ferrocenylacetylene (1.05 g.) in 10 ml. absolute THF was treated with 2.6 ml. of a solution of BuLi in heptane under N, after 15 min. a solution of 1.10 g. ferrocenylcarboxaldehyde in 15 ml. THF added dropwise and the mixture stirred 1 hr. at room temperature and worked up to give 1, 3-diferrocenylpropynone (XII) and after recrystallization, 1, 3-diferrocenylpropynol (XIII), m. 142-52° ( $\text{CH}_2\text{Cl}_2$ ). The crude mixture of XII and XIII was oxidized with 5 g.  $\text{MnO}_2$  in 30 ml.  $\text{CHCl}_3$  1 hr. and worked up to give 63 percent XII, m. 166-8° (cyclohexane- $\text{C}_6\text{H}_6$ ). Crude XIII (0.76 g.) in 20 ml. absolute THF was added to a mixture of 0.1 g.  $\text{LiAlH}_4$  and 0.35 g.  $\text{AlCl}_3$  in 10 ml. absolute  $\text{Et}_2\text{O}$ , the mixture stirred 15 min. and worked up to give 56 percent 1, 3-diferrocenylpropyne. Oxidation of the Li salt of ferrocenylacetylene and 3-ferrocenylpropenal with  $\text{MnO}_2$  gave 90 percent 1, 5-diferrocenyl-1-penten-4-yn-3-one, m. 92-5° ( $\text{C}_6\text{H}_6$ -cyclohexane). The infrared and ultraviolet spectra of the compounds were discussed.

214. Nakamura, A., Kim, P., and Hagihara, N.,  
 INTERACTION OF CUMULENE SYSTEMS WITH ORGANO-  
 METALLIC  $\pi$ -COMPLEXES. II. FERROCENYLBUTA-  
 TRIENES AND RELATED COMPOUNDS, Journal of  
Organometallic Chemistry, Vol. 3, No. 5, 1965, pp. 355-  
 363 (cf. CA 62, 11852f).

Ferrocenylbutatrienes and corresponding butadiene derivatives were prepared and their electronic spectra were measured. There was considerable difficulty in obtaining pure samples. (Tetraphenylallene)- and (tetraphenylbutatriene) chromium tricarbonyls were also prepared. Absorption bands due to a charge transfer from the metal into the butatriene system were observed and thought to be in a close relationship to the stabilization of the butatriene system by neighboring ferrocenyl groups.

215. Pauson, P. L. and Watts, W. E.,  
FERROCENE DERIVATIVES. XIII. SOME FERROCENYL-  
ETHYLENE AND ACETYLENE DERIVATIVES, Chemical  
Society Journal, 1963, pp. 2990-2996 (cf. CA 57, 16650f).

Ferrocenecarboxaldehyde and benzoylferrocene have been converted into 1, 2-diferrocenylethylene derivatives; and (ferrocenylmethylene) triphenylphosphorane ( $\text{FcCH:PPH}_3$ , Fc = ferrocenyl) has been used for the preparation of a range of ferrocene olefins and acetylenes.

216. Purdue University, Lafayette, Indiana  
ALPHA-HALOFERROCENES. THE SYNTHESIS OF  
FERROCENYLACETYLENE by R. A. Benkeser and  
W. P. Fitzgerald, May 1961, Report No. AFOSR-787,  
AD-440 519, Contract No. AF 49(638)-297 (Unclassified  
Report) (Journal of Organic Chemistry, Vol. 26, 1961,  
pp. 4179-4180).

The syntheses of alpha-chloroferrocene, alphabromoethylferrocene, alpha, beta-dibromoethylferrocene, and ferrocenylacetylene are reported. The alphachloroethylferrocene was prepared by adding dry hydrogen chloride to vinylferrocene in pentane at  $-78^\circ\text{C}$  and recrystallization. This compound was also prepared by treating an ethereal solution of alphahydroxyethylferrocene containing activated alumina with anhydrous hydrogen chloride. The alpha-bromoethylferrocene was prepared by adding anhydrous hydrogen bromide to vinylferrocene in pentane at  $-78^\circ\text{C}$ .

Bromine was added to vinylferrocene in pentane at  $-78^\circ\text{C}$  to form the alpha, beta-dibromoethylferrocene. Ferrocenylacetylene was prepared by adding a solution to the dibromide in pentane to potassium amide in liquid ammonia.

217. Rausch, M. D., Siegel, A., and Klemann, L. P.,  
A FACILE ROUTE TO FERROCENYL- AND 2-THIENYLARY-  
LACETYLENES, Journal of Organic Chemistry, Vol. 31,  
1966, p. 2703.

Stephens and Oastro have recently described a useful new synthesis for tolane (diphenylacetylene) and substituted tolanes utilizing aryl iodides and cuprous phenylacetylide in refluxing pyridine (R. D. Stephens and C. E. Oastro, Journal of Organic Chemistry, Vol. 28, 1963, p. 3313). It

was of interest to us to determine if this procedure could be employed for the formation of ferrocenyl and certain heterocyclic arylacetylenes, and to study the chemistry of these substances. Our preliminary studies have been successful, and are reported in this article.

218. Schlogel, K. and Egger, H.,  
FERROCENE DERIVATIVES. XVIII. SYNTHESIS OF  
FERROCENYLPOLYENES, XIX. LIGHT ABSORPTION OF  
FERROCENYLPOLYENES, Ann., Vol. 676, 1964, pp. 76-  
97 (cf. CA 59, 7557f, CA 59, 8787f, CA 60, 13269g, CA 61,  
7041h).

#### XVIII

Fc = ferrocenyl throughout this abstract.

FcCHO (I) was converted by chain-lengthening with EtOC:CH (II) or MeOCH:CHC:CH (III) into a series of vinylogous Fc(CH:CH)<sub>n</sub>R (R = CHO, n = 1-4) (IV). IV yielded by Knoevenagel condensations polyenemono- and dicarboxylic acid esters and by Wittig reactions with phosphorylenes, a series of Fc(CH:CH)<sub>n</sub>R (V) (R = Ph, Fc, 2-thienyl, and aryl, n = 1-5 and 7), which were also obtained from FcCH:PPh<sub>3</sub> (VI) and phenylpolyenals. The properties of the ferrocenylpolyenes were compared with those of the phenylpolyenes. III (3.7 g.) in 10 cc. tetrahydrofuran (THF) added dropwise with stirring at 40° under N to PtMgBr from 1.1 g. Mg and 4.9 g. EtBr in 30 cc. dry THF, kept 1 hr. at 20°, treated dropwise with stirring at room temperature with 8.6 g. I in 40 cc. THF, warmed after 1 hr. to 50-60°, stirred 2 hrs. at 50-60°, cooled to 0°, treated dropwise with 2 cc. absolute EtOH and after 10 min. with 1.6 g. LiAlH<sub>4</sub> in portions during 20 min., and stirred 15 hrs. at room temperature yielded 47 percent Fc(CH:CH)<sub>2</sub>CHO (VII), m. 135-6° (C<sub>6</sub>H<sub>6</sub>-petr. ether); semicarbazone m. 207-8° (decomposition). Similarly was prepared 31 percent FcCH:-CHCHO (VIII), m. 94-6° (petr. ether) [semicarbazone m. 180° (decomposition)], from I and II. VIII was also obtained in 35 percent yield by oxidizing FcCH:CHCH<sub>2</sub>OH in CHCl<sub>3</sub> with MnO<sub>2</sub> during 8-10 hrs. III in dry THF treated under N with one equivalent PhLi in Et<sub>2</sub>O, stirred 1 hr. at room temperature, and then treated 2 hrs. at room temperature with VIII or VII yielded 19 percent Fc(CH:CH)<sub>3</sub>CHO (IX), m. 185-7° (decomposition) (semicarbazone carbonizes from 250° on),

or 26 percent  $\text{Fc}(\text{CH}:\text{CH})_4\text{CHO}$  (X), m.  $255^\circ$  (decomposition) ( $\text{C}_6\text{H}_6$ ) (semicarbazone carbonizes from  $250^\circ$  on). The appropriate IV (2-5 millimoles) and 2 mole-equivalents powered  $\text{CH}_2(\text{CO}_2\text{H})_2$  in 5-10 cc. dry  $\text{C}_5\text{H}_5\text{N}$  and a few drops piperidine heated 2-3 hrs. on a water bath, and the crude product refluxed 1 hr. in 10-20 cc. xylene and then treated with  $\text{CH}_2\text{N}_2\text{-Et}_2\text{O}$  yielded the corresponding  $\text{Fc}(\text{CH}:\text{CH})_n\text{-CO}_2\text{Me}$  (n and melting point given); 1,  $102\text{-}3^\circ$  (aqueous MeOH); 2,  $141\text{-}3^\circ$  (petr. ether); 3,  $174\text{-}5^\circ$  ( $\text{C}_6\text{H}_6$ -petr. ether); 4,  $192\text{-}4^\circ$  (decomposition) ( $\text{C}_6\text{H}_6$ -petr. ether); 5,  $206\text{-}9^\circ$  (decomposition) ( $\text{C}_6\text{H}_6$ -petr. ether). I and  $\text{CH}_2(\text{CO}_2\text{H})_2$  in  $\text{CH}_2\text{-Cl}_2$  refluxed 6 hrs. with a little piperidine acetate and the crude product treated with  $\text{CH}_2\text{N}_2\text{-Et}_2\text{O}$  yielded 22 percent  $\text{FcCH}:\text{C}(\text{CO}_2\text{Me})_2$ , b<sub>0.0001</sub>  $120\text{-}30^\circ$ , m.  $97\text{-}8^\circ$  (petr. ether). Similarly were prepared from the appropriate IV the following  $\text{Fc}(\text{CH}:\text{CH})_n\text{CH}:\text{C}(\text{CO}_2\text{Me})_2$  (n and melting point given): 1,  $56\text{-}9^\circ$  (petr. ether); 2,  $115\text{-}16^\circ$  (cyclohexane); 3,  $155\text{-}8^\circ$  (cyclohexane- $\text{C}_6\text{H}_6$ ) (18 percent yield); 3,  $185\text{-}7^\circ$  (decomposition) ( $\text{C}_6\text{H}_6$ -petr. ether) (34 percent yield). 2-Thienyl chloride and one equivalent  $\text{PPh}_3$  heated 20 min. on a water bath gave nearly quantitative 2-thienyltriphenylphosphonium chloride (XI), m.  $310\text{-}11^\circ$  (decomposition). ( $:\text{CCH}_2\text{Br}$ )<sub>2</sub> (4.3 g.) and 12 g.  $\text{PPh}_3$  in 40 cc.  $\text{MeNO}_2$  heated 0.5 hr. on a water bath yielded 14 g. [ $:\text{CCH}_2\text{PPh}_3$ ]  $\text{Br}_2$  (XII), m.  $220\text{-}4^\circ$  (decomposition); a 1:1 ratio of the reactants gave similarly [ $\text{BrCH}_2\text{C}:\text{CCH}_2\text{PPh}_3$ ]  $\text{Br}$ , m.  $179\text{-}82^\circ$ . The appropriate phosphonium salt (2-5 millimoles) and a suitable aldehyde in 10-30 cc. absolute EtOH treated with 1.1 equivalent Li as a 0.2N solution in absolute EtOH and stirred 2-3 hrs. at  $50\text{-}60^\circ$  under N gave the corresponding trans- $\text{Fc}(\text{CH}:\text{CH})_n\text{R}$  (XIII); the residue from the mother liquor, containing the cis isomers, heated with a little p- $\text{MeC}_6\text{H}_4\text{SO}_3\text{H}$  gave additional XIII (method A); the isomers could be separated by thin-layer chromatography. The appropriate phosphonium salt in dry THF treated under N with about 10 percent excess M  $\text{PhLi-Et}_2\text{O}$  (method B) or  $\text{BuLi-Et}_2\text{O}$  (method C), stirred 1 hr. at room temperature, and treated slowly dropwise with the aldehyde in THF, and the mixture worked up in the usual manner gave the corresponding XIII (R, n, percent yield, melting point, method, and aldehyde used are given): Ph (XIV), 1, 40 (80 percent cis-trans isomer mixture),  $122\text{-}3^\circ$  (petr. ether) (cis isomer m.  $44\text{-}6^\circ$ ), B, BzH; 2-thienyl, 1, — (41 percent cis-trans isomer mixture),  $151\text{-}2^\circ$  (petr. ether)

[cis isomer m. 68-70° (petr. ether)], A, 2-thienal [80 percent 1:1 cis-trans isomer mixture from XI and I by method B]; Fc, 1 (XV), 26, ~270° (decomposition), B, I; Ph, 2, — (46 percent cis-trans isomer mixture), 194-5° (petr. ether), A, PhCH:CHCHO; 2-thienyl, 2, — (63 percent cis-trans isomer mixture), 176-8° (decomposition) (C<sub>6</sub>H<sub>6</sub>-petr. ether), A, VIII; Fc, 2 (XVI), 25, — (carbonizes), B, VIII; p-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>, 2, — (71 percent cis-trans isomer mixture), 199-200° (cyclohexane-C<sub>6</sub>H<sub>6</sub>), C, p-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CH:CHCHO; p-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>, 2, — (57 percent cis-trans isomer mixture), 188-90° (cyclohexane), C, p-Me<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>CH:CHCHO; Ph, 3, 23, 213-15° (decomposition) (petr. ether), A, Ph(CH:CH)<sub>2</sub>CHO; 2-thienyl, 3, 36, 194-6° (decomposition) (C<sub>6</sub>H<sub>6</sub>-petr. ether), A VII; Fc, 3 (XVII), 17, — (carbonizes), A, VII; Ph, 4, 26, 228-30° (decomposition) (C<sub>6</sub>H<sub>6</sub>), B, Ph(CH:CH)<sub>3</sub>CHO; Fc, 4 (XVIII), 42, — (carbonizes), B, OHC(CH:CH)<sub>2</sub>CHO; Ph, 5, 13, — (carbonizes), B, Ph(CH:CH)<sub>4</sub>CHO; Fc, (XIX), ~5, — (carbonizes), B, X; Ph, 7, ~5, — (carbonizes), B, Ph(CH:CH)<sub>4</sub>CHO. Ferrocene-1, 1'-dicarboxaldehyde and VI gave by method B orange 1, 1'-bis (2-ferrocenylvinyl) ferrocene, did not melt up to 250°. BuLi, XII, and I gave by method C a trace of cis, cis-1, 6-diferrocenyl-1, 5-hexadien-3-yne and the red trans, trans isomer (XX), carbonizes at about 250°. XX in cyclohexane hydrogenated over Lindlar catalyst, and the product treated with p-MeC<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>H yielded XVII. VIII with N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O gave dark red (FcCH:CHCH:N)<sub>2</sub>, decomposition above 240° (CH<sub>2</sub>Cl<sub>2</sub>).

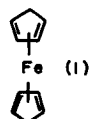
## XIX

The absorption spectra (recorded) of VII, VIII, IX, X, XV, XVI, XVII, XVIII, and XIX between 250 and 550 mμ were compared with those of the corresponding phenyl-polyenes. The mutual electronic effects between the ferrocene nucleus and the polyene system cause a bathochromic shift of the  $\pi \rightarrow \pi^*$  bands lowering of the oscillator strengths, and loss of the fine structure of the bands with the replacement of the Ph by Fc. The effects of the groups R in Fc-(CH:CH)<sub>n</sub>R, of the replacement of CH by N in the polyene chain, and of the solvents on the spectra is discussed.



219. Schlogel K. and Egger, H.,  
SYNTHESIS AND REACTION OF FERROCENYLACETYLENE,  
Monatshefte, Vol. 94, No. 2, 1963, pp. 376-392.

A Friedel-Crafts acylation of 9.3 g. ferrocene (I) with 9 g.  $\text{Cl}_2\text{CHCOCl}$  in  $\text{CH}_2\text{Cl}_2$  gave, after conventional workup and chromatography on  $\text{Al}_2\text{O}_3$ , 1.6 g. dark red needles of dichloroacetylferrocene (II) m.  $93-4^\circ$  (petr. ether), and 0.7



g. orange-red chloroacetylferrocene (III), m.  $92-3^\circ$ . III was also obtained, in higher yield, by an analogous acylation of I with  $\text{ClCH}_2\text{COCl}$ . An attempted acylation of I with  $\text{Cl}_3\text{CCOCl}$  gave II in 25 percent yield.  $\text{LiAlH}_4$  reduction of 1.5 g. III in  $\text{Et}_2\text{O}$  at  $-10^\circ$  gave 1.5 g. yellow crystals of 1-hydroxy-2-chloroethylferrocene (IV), m.  $76-7^\circ$  (petr. ether). A similar reduction of II gave 1-hydroxy-2, 2-dichloroethylferrocene (V), m.  $68-71^\circ$  (petr. ether).  $\text{LiAlH}_4\text{-AlCl}_3$  reduction of III gave, after separation of products of thin-layer chromatography (TLC), 53 percent IV, yellow plates of 23 percent 2-chloroethylferrocene, m.  $52-4^\circ$  (petr. ether), and a trace of ethylferrocene (VI). A similar reduction of 2.55 g. II gave 1.18 g. V, 0.1 g. VI, 0.64 g. 2, 2-dichloroethylferrocene (VII), m.  $81-2^\circ$  (petr. ether), and yellow-orange 0.22 g. bis (1-ferrocenyl-2-chloroethyl) ether, m.  $45-7^\circ$  ( $\text{MeOH-H}_2\text{O}$ ). Dehydration of 0.8 g. IV with acidic  $\text{Al}_2\text{O}_3$  in  $\text{C}_6\text{H}_6$  gave 0.57 g. 2-chlorovinylferrocene (VIII). Similar treatment of 0.3 g. II gave 0.06 g. 2, 2-dichlorovinylferrocene as orange-yellow crystals m.  $55-8^\circ$ .  $\text{HCl}$  abstraction from 0.57 g. VIII with  $\text{NaNH}_2$  in liquid  $\text{NH}_3$  gave 0.27 g. ferrocenylacetylene (IX), m.  $55-6^\circ$ . Similar treatment of VII also gave IX. IX (0.1 g.), refluxed with  $\text{Cu}(\text{OAc})_2$  and pyridine, gave 0.09 g. 1, 4-diferrocenylbutadiyne (X) as orange rods, m.  $196-8^\circ$  (decomposition) (petr. ether). X was also obtained by coupling IX with  $\text{NaNH}_2$  in liquid  $\text{NH}_3$ . A mixed coupling reaction between IX and  $\text{PhC}\equiv\text{CH}$  gave, after separation of products by TLC: X,  $\text{PhC}\equiv\text{CC}\equiv\text{CPh}$ , and 50 percent 1-ferrocenyl-4-phenylbutadiyne (XI) as orange needles,

m. 112-13° (petr. ether). Reduction of XI with H over 10 percent Pd-C in EtOAc gave 1-ferrocenyl-4-phenylbutane as yellow plates, m. 106-8° (petr. ether). A similar reduction of X gave 1, 4-diferrocenylbutane. Oxidation of IX with HgSO<sub>4</sub> in 10 percent H<sub>2</sub>SO<sub>4</sub> gave 70 percent methyl ferrocenyl ketone, m. 83-5° (petr. ether). Stirring 0.13 g. IV with NaOH in Et<sub>2</sub>O gave 0.08 g. 1, 2-dihydroxyethylferrocene (XII) as dark yellow crystals, m. 148-52° (decomposition). Reduction of XII with LiAlH<sub>4</sub>-AlCl<sub>3</sub> in tetrahydrofuran gave 2-hydroxyethylferrocene, m. 32-3° (petr. ether). Heating 0.18 g. IV with Na in EtOH gave 0.06 g. 2-ferrocenylvinyl ferrocenyl ketone (XIII), m. 207-10° (decomposition). Reduction of XIII with H over 10 percent Pd-C in EtOAc gave orange crystals of 2-ferrocenylethyl ferrocenyl ketone (XIV), m. 127-30° (C<sub>6</sub>H<sub>6</sub>). Reduction of XIII with H over PtO<sub>2</sub> in HOAc gave 1, 3-diferrocenylpropane as yellow plates, m. 87-9° (petr. ether).

220. Schlogel, K. and Mohar, A.,  
FERROCENE DERIVATIVES. XI. FERROCENYLACETYLENES. 2. PREPARATION AND REACTIONS OF FERROCENYLALKYNES AND ALKYNYL KETONES, Monatshefte, Vol. 93, 1962, pp. 861-876 (cf. CA 55, 27245c, CA 56, 15545h, and CA 57, 15151a).

Fc = ferrocenyl throughout this abstract. A series of new, unsaturated ferrocene derivatives was prepared from ferrocenylacetylene carbinols and glycols by partial catalytic reduction, reduction with LiAlH<sub>4</sub>-AlCl<sub>3</sub>, and by oxidation with MnO<sub>2</sub>. FcCOC:CH (I) was converted to heterocyclic ferrocene derivatives (FcCH:CH)<sub>2</sub> (II) and FcCH:CHCH:CHPh (III) were prepared and their ultraviolet spectra compared with that of (PhCH:CH)<sub>2</sub> (IV). The attempted synthesis of higher unsaturated systems (hexatrienes and cumulenes) did not give any conclusive results. FcCH:C:CH<sub>2</sub> (V) and FcCH:C:CHPh (VI), as well as FcCH:-CHCHO (VII), were prepared by the base- and acid-catalyzed rearrangement of suitable, unsaturated ferrocenyl derivatives. FcCH(OH)C:CH (VIII) (1.0 g.) in EtOH hydrogenated over 0.2 g. Lindlar catalyst until 101 cc. H had been absorbed, filtered, and evaporated at 30°, and the residue distilled yielded 0.83 g. FcCH(OH)CH:CH<sub>2</sub> (IX) yellow oil, b<sub>0.3</sub> 105-15° (bath). FcMeC(OH)C:CH yielded similarly 75 percent

$\text{FcMeC(OH)CH:CH}_2$ ,  $b_{0.2}$  100-10° (bath).  $\text{FcCH(OH)C:CPh}$  (X) in EtOH hydrogenated over Lindlar catalyst yielded 70 percent cis- $\text{FcCH(OH)CH:CHPh}$  (XI), m. 78-80° (petr. ether), which, hydrogenated further over Pd-C in EtOH, yielded the oily, yellow  $\text{FcCH(OH)CH}_2\text{CH}_2\text{Ph}$  (XII),  $b_{0.3}$  140-5° (bath). X (0.8 g.) in 50 cc. dry  $\text{Et}_2\text{O}$  refluxed 4 hrs. with 0.09 g.  $\text{LiAlH}_4$  and worked up yielded 0.5 g. trans isomer (XIII) of XI, m. 56-63°, which, hydrogenated over Pd-C in EtOH, gave XII. VIII (2.40 g.) in 40 cc. dry  $\text{Et}_2\text{O}$  added dropwise with stirring to 0.38 g.  $\text{LiAlH}_4$  and 1.33 g.  $\text{AlCl}_3$  in 30 cc. dry  $\text{Et}_2\text{O}$ , stirred 20 min. at room temperature, and worked up, and the crude product chromatographed on  $\text{Al}_2\text{O}_3$  gave 1.8 g. yellow, oily  $\text{FcCH}_2\text{C:CCH}$  (XIV),  $b_{10}$  90-100° (bath). XIV (0.5 g.) added dropwise with cooling to 3.3 g. KI in 3.3 cc.  $\text{H}_2\text{O}$  and 1.35 g.  $\text{HgCl}_2$  in 2.6 cc. 10 percent aqueous NaOH gave the Hg derivative, m. 175-8° ( $\text{C}_6\text{H}_6$ -petr. ether). XIV hydrogenated in EtOH over Pd-C gave nearly 100 percent FcPr. In a similar manner as XIV, were prepared the following compounds:  $\text{FcCHMeC:CCH}$ , orange oil,  $b_{10}$  100-20°, 74 percent (hydrogenated to F Bu) [it gave an Hg derivative, m. 169-72° ( $\text{C}_6\text{H}_6$ -petr. ether)];  $\text{FcCH}_2\text{C:CPh}$  (XV), m. 79-81° (petr. ether), 45 percent [hydrogenated to  $\text{Fc(CH}_2)_3\text{Ph}$  (XVI), yellow oil,  $b_{0.3}$  90-100° (bath)];  $(\text{FcCH}_2\text{C:})_2$ , m. 105-8° (EtOH), 42 percent [hydrogenated to  $(\text{FcCH}_2\text{CH}_2)_2$  (XVII), m. 106-11° (petr. ether)];  $(\text{FcCH}_2\text{C:C})_2$ , m. 126-34° (aqueous EtOH), 57 percent (impure) [it gave (hydrogenated in cyclohexane over Pd-C) 80 percent  $[\text{Fc(CH}_2)_3]_2$  (XVIII), m. 112-17° (chromatographed on  $\text{Al}_2\text{O}_3$  and recrystallized from petr. ether)].  $\text{FcCH(OH)C:CCH(OH)Ph}$  (0.3 g.) in 40 cc. dry  $\text{Et}_2\text{O}$  refluxed 4 hrs. with 0.5 g.  $\text{LiAlH}_4$  and worked up, and the crude product chromatographed on  $\text{Al}_2\text{O}_3$  yielded 0.16 g. III, m. 189-91° (decomposition) (petr. ether).  $\text{FcCH(OH)C:C}$  (XIX) (0.7 g.) in 15 cc. dry tetrahydrofuran added dropwise with stirring to 0.7 g.  $\text{LiAlH}_4$  in 20 cc. tetrahydrofuran, refluxed 3 hrs., and worked up gave 0.1 g. sparingly soluble solid, probably  $[\text{FcCH(OH)-CH:CH}]_2$ , and 0.3 g.  $\text{Fc(CH:CH)}_3\text{F}$  (XIXa), which, hydrogenated in EtOH over Pd-C, gave XVIII. The appropriate carbinol or glycol in  $\text{CHCl}_3$  treated at room temperature with 2-3 parts activated  $\text{MnO}_2$ , kept 1-24 hrs. with occasional shaking at room temperature, filtered, and evaporated, and the residue chromatographed on  $\text{Al}_2\text{O}_3$  yielded usually more than 70 percent corresponding ketone. In this manner were

prepared the following compounds (melting point given): I, 78-80° (C<sub>6</sub>H<sub>6</sub>-petr. ether); FcCOCH:CH<sub>2</sub>, 65-9° (petr. ether); FcCOC:CPh, 103-6° (EtOH); cis-FcCOCH:CHPh, 130-1° (EtOH); trans-FcCOCH:CHPh, 139-40° (EtOH); FcCOCH<sub>2</sub>CH<sub>2</sub>-Ph, 85-6° (petr. ether); FcCOC:CCOFc, 158-61° (C<sub>6</sub>H<sub>6</sub>-petr. ether); (FcCOC:C)<sub>2</sub>, 161-4° (C<sub>6</sub>H<sub>6</sub>-petr. ether). I (1.19 g.) in 20 cc. EtOH and 0.35 g. NH<sub>2</sub>OH.HCl heated 12 hrs. on the water bath, treated with a saturated aqueous solution of 0.5 g. Na<sub>2</sub>CO<sub>3</sub>, heated 1 hr., diluted with H<sub>2</sub>O, and extracted with Et<sub>2</sub>O, and the residue from the extract chromatographed on Al<sub>2</sub>O<sub>3</sub> gave 0.2 g. ferrocenylisoxazole (XX), m. 93-5° (aqueous EtOH). A similar run with a reflux period of only 1 hr. yielded 34 percent isomer of XX, m. 110-12° (aqueous EtOH). N<sub>2</sub>H<sub>4</sub>.H<sub>2</sub>SO<sub>4</sub> (0.16 g.) and 0.3 g. I in 20 cc. 90 percent aqueous EtOH refluxed 2 hrs., treated with 0.12 g. Na<sub>2</sub>CO<sub>3</sub> as a saturated aqueous solution, heated 45 min., concentrated, diluted with H<sub>2</sub>O, and extracted with Et<sub>2</sub>O, and the residue from the extract chromatographed on Al<sub>2</sub>O<sub>3</sub> gave 0.27 g. 3-ferrocenylpyrazole, m. 148-52° (C<sub>6</sub>H<sub>6</sub>). XIV in petr. ether chromatographed on strongly alkaline Al<sub>2</sub>O<sub>3</sub> yielded about equal parts of FcC:CMe (XXI), m. 86-8° (EtOH), and oily V, b<sub>10</sub> about 100° (bath) (partial decomposition), which, refrigerated 2 weeks, was contaminated with XXI and VIII and larger amounts insoluble products. XV isomerized in the same manner on strongly alkaline Al<sub>2</sub>O<sub>3</sub> gave VI, m. 98-100° (EtOH), which was contaminated after a short while again with XV. The catalytic hydrogenation of XV and VI yielded XVI. XV and VI oxidized with MnO<sub>2</sub> in CHCl<sub>3</sub> yielded FcCOC:CPh. XIII (0.2 g.), 2.0 g. KOH, and 10 cc. EtOH refluxed 3 hrs., diluted with H<sub>2</sub>O, and extracted with Et<sub>2</sub>O, and the residue from the extract chromatographed on Al<sub>2</sub>O<sub>3</sub> yielded 0.05 g. FcCOCH<sub>2</sub>CH<sub>2</sub>Ph (XXII), m. 85-6°. XI gave similarly 2-5 percent XXII. IX treated with alcoholic KOH yielded traces of FcCOEt. VIII (0.6 g.) in 5 cc. dioxane and 2 cc. 90 percent HCO<sub>2</sub>H heated a few min. on the water bath, diluted with H<sub>2</sub>O, and extracted with Et<sub>2</sub>O and the residue from the extract separated by preparative thin-layer chromatography with silica gel gave 0.28 g. VII, m. 90-5°; semicarbazone decomposing at about 180°, with discoloration from 110° on. VII in dry Et<sub>2</sub>O reduced with LiAlH<sub>4</sub> gave FcCH:CHCH<sub>2</sub>OH (XXIII), m. 66-9° (C<sub>6</sub>H<sub>6</sub>-petr. ether). IX (0.35 g.) in 25 cc. dioxane heated 2 hrs. on the water bath with 10 cc. N HCl yielded 0.20 g. semisolid, R<sub>f</sub> 0.9 (C<sub>6</sub>H<sub>6</sub>),

0.54 (petr. ether), containing traces of XXIII; the crude product hydrogenated in EtOH over Pd-C and then treated with  $\text{LiAlH}_4$  and  $\text{AlCl}_3$  gave FcPr. The ultraviolet absorption spectra of II, III, IV, and XIXa were given.

221. Schlogel, K. and Steyrer, W.,  
FERROCENE DERIVATIVES. XXVII. FERROCENE ACETYLENES, 5. GENERAL METHOD FOR THE PREPARATION OF FERROCENE ACETYLENES AND FERROCENE ALLENES, Montashefte fuer Chemie, Vol. 96, No. 5, 1945, pp. 1520-1535 (In German) (cf. CA 63, 9984c).

Acylferrocenes with the Vilsmeier complex from  $\text{HCONMe}_2$  and  $\text{POCl}_3$  yielded by formylation of the primarily formed  $\alpha$ -chlorovinylferrocenes the ferrocenylchloroacroleins (I). Fc = ferrocenyl throughout this abstract. The I gave by dehydrochlorination and fragmentation the corresponding isomeric  $\text{FcC:CR}$  (II) and  $\text{Fc}(\text{CH}_2)_n\text{C:CH}$  (III) and the ferrocenylallenes, respectively. This general method, which can also be extended to 1, 1'-disubstituted ferrocenes, was especially suitable for the preparation of II (R = H) (IV). The intermediates offer several preparative possibilities, some of which were explored. During the course of elucidating the mechanism of the chloroformylation, ethynylcyclopentadienylmanganese tricarbonyl (V) was prepared for the first time.  $\text{POCl}_3$  (14 cc.) added dropwise with stirring and cooling to 7 cc.  $\text{HCONMe}_2$ , stirred 0.5 hr. at room temperature, added to 5.5 g.  $\text{Ph}_3\text{PC}(\text{CO}_2\text{Et})\text{COFc}$ , and kept 23 hrs. at  $20^\circ$ , and the product treated 45 min. with 100 cc. 10 percent NaOH-MeOH and 10 percent aqueous NaOH yielded 1.73 g.  $\text{FcC:CCO}_2\text{H}$  (VI), m.  $108-12^\circ$  (decomposition) (all melting points were determined on the Kofler Block). VI in  $\text{Et}_2\text{O}$  treated 3 min. with cooling with  $\text{CH}_2\text{N}_2$ - $\text{Et}_2\text{O}$  yielded 1.73 g. orange Me ester of VI, m.  $120-1^\circ$  (petroleum ether). VI and a trace of Cu powder distilled at  $130-50^\circ/0.3$  mm. gave nearly quantitative IV, m.  $55-6^\circ$ ; runs with 1-2 g. VI gave similarly 60-70 percent IV. VI (72 mg.), 3 cc. MeOH, 4 cc. dry  $\text{C}_5\text{H}_5\text{N}$ , and 0.3 g. powdered  $\text{Cu}(\text{OAc})_2$  refluxed 0.5 hr., and the crude product treated with N HCl and extracted with  $\text{CH}_2\text{Cl}_2$  yielded 56 mg.  $\text{Fc}(\text{C:C})_2\text{Fc}$ . Ferrocene (VII) and the BzCl in  $\text{CH}_2\text{Cl}_2$  refluxed 5 hrs. with  $\text{AlCl}_3$  yielded 60-80 percent  $\text{FcCOCHPh}$ , m.  $128-9^\circ$  (petroleum ether). VII with thenoyl chloride gave similarly during 45 min. at  $5^\circ$  2-ferrocenylmethylthiophene

(VIII), m. 93-6° (petroleum ether). Ferrocenoylmethylferrocene, m. 127-30° (petroleum ether), was obtained similarly at 20° during 45 min. (EtMeCHCO)<sub>2</sub>O, VII and Et<sub>2</sub>O-BF<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub> kept 24 hrs. at 20° yielded FcCOCHEtMe, b<sub>0.001</sub> 85-90°. VIII was oxidized rapidly on Al<sub>2</sub>O<sub>3</sub> columns to ferrocenyl thienyl diketone, m. 91-2°. POCl<sub>3</sub> (0.18 cc.) added with stirring and cooling to 0.3 cc. HCONMe<sub>2</sub> during 3-5 min., stirred 0.5 hr., treated with 1 millimole FcAc, and stirred for 10 min. at 20° crude product chromatographed yielded FcCCl:CH<sub>2</sub>, m. 49-50°. Similarly were prepared the FcCCl:CRR' (IX) listed in the first table. IV treated similarly 0.5 hr. at room temperature with POCl<sub>3</sub>-HCONMe<sub>2</sub>

R	R'	Reaction		Yield	mp or bp/mm.
		Time (min)	Temp		
Me	H (X)	25	20°	87	90°/0.001
Et	H (XI)	45	20°	85	65°/0.001
Ph	H	180	20°	38	82-3°
2-thienyl	H	45	5°	7	117-18°
FcCH <sub>2</sub>	H	180	20°	51	108-10°
Et	Me	80	50°	92	100°/0.001

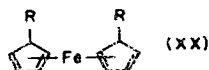
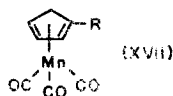
gave nearly quantitative a mixture of cis- and trans-FcCCl:-CHCHO (XII), m. 78-9° (petroleum ether); a similar run worked up after 1 min. gave an additional small amount of FcC:CCHO, m. 78-9°. FeCH:CH<sub>2</sub> gave similarly nearly quantitative FcCH:CHCHO. In the same manner, as described for the IX were prepared the FeCCl:C(CHO)R (XIII) listed in the second table. XII (0.27 g.) in 15 cc. absolute EtOH added dropwise during 10 min. at 30-40° with stirring to

R	Reaction		Yield	mp
	Time (hrs)	Temp		
Me (XIV)	1	60°	90	79-80°
Ph	3	60°	74	104-25° (cis-trans mixt)
2-thienyl (XIVa)	0.75	5°	66	100-15° (cis-trans mixt)
FeCH <sub>2</sub>	3	20°	7 (cis)	129-31°
			5 (trans)	156-8°

0.35 g. Na in 15 cc. absolute EtOH, kept 20 min., and stirred into about 100 cc. H<sub>2</sub>O gave 64 percent orange FcC(OEt):CHCHO (XV), m. 90-1° (petroleum ether-C<sub>6</sub>H<sub>6</sub>). XV (0.1 g.) in 2 cc. MeOH heated 1 hr. on a water bath with 3.5 mg. p-MeC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>Cl yielded 0.074 g. FcCOCH<sub>2</sub>CH(OMe)<sub>2</sub>, m. 57-8° (petroleum ether). XV (0.1 g.) and 70 mg. N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>SO<sub>4</sub> in 15 cc. 90 percent EtOH heated 2 hrs. on a water bath, treated with saturated aqueous Na<sub>2</sub>CO<sub>3</sub>, and heated 45 min. gave 0.062 g. 3-ferrocenylpyrazole, m. 147-9°. XII (0.27 g.) in 7 cc. Me<sub>2</sub>CO added dropwise during 10 min. to 0.8 g. KOH in 15 cc. H<sub>2</sub>O and Me<sub>2</sub>CO 15 cc. at 40-50° and stirred 5 min. gave 0.29 g. FcCCl:CHCH:CHAc, m. 111-13° (petroleum ether). The appropriate IX or XIII (3 millimoles) added dropwise with stirring to NaNH<sub>2</sub> from 2 g. Na in 100 cc. liquid NH<sub>3</sub> and stirred 15-60 min. yielded the corresponding II (method A). NaH (0.010 mole) in Me<sub>2</sub>SO treated with cooling and stirring with H<sub>2</sub>O until the H evolution ceased, treated with 1 millimole appropriate IX or XIII in Me<sub>2</sub>SO and stirred 3-8 hrs. at 40-70° gave the corresponding II (method B). The II prepared by these methods are listed in the third table. FcAc (4 g.), 5.39 cc. HCONMe<sub>2</sub>, and 3.9 cc. POCl<sub>3</sub>

R	Method	Yield %	mp or bp/mm.
H	A	90	55-6° (petroleum ether)
	A	80	
Me	B	75	86-8° (EtOH)
	B	35	
Et (XVI)	B	83	38-40° (EtOH)
			75-80°/0.001
Ph	A	88	126-8° (petroleum ether)
	A	81	
2-thienyl	A	11	108-10° (petroleum ether)
	A	15	

heated 4 hrs. at 50° yielded 4.4 g. XII. XII (4.4 g.) in about 100 cc. dry Et<sub>2</sub>O stirred 45 min. with NaNH<sub>2</sub> in liquid NH<sub>3</sub> gave 2.7 g. IV, m. 55-6°. XVII (R = Ac) (1 g.), 1.25 cc. HCONMe<sub>2</sub>, and 0.74 cc. POCl<sub>3</sub> stirred 3 hrs. at room



temperature in the dark yielded 0.6 g. yellow XVII ( $R = \text{CCl:CHCHO}$ ) (XVIII), m.  $107-8^\circ$  (petroleum ether). XVIII (0.4 g.) treated 0.5 hr. by method A with  $\text{NaNH}_2$  in liquid  $\text{NH}_3$  yielded 0.18 g. V. V in MeOH with an alkaline solution of  $\text{K}_2\text{HgI}_4$  yielded the light yellow Hg derivative, decomposed at  $205-12^\circ$ . V (77 mg.) treated 70 min. with  $\text{Cu}(\text{OAc})_2$  yielded 65 mg. 1, 4-bis (cyclopentadienylmanganesetri-carbonyl) butadiyne, m.  $148-50^\circ$  (petroleum ether- $\text{C}_6\text{H}_6$ ). X (0.62 g.) treated 0.5 hr. with  $\text{NaNH}_2$  in liquid  $\text{NH}_3$  yielded 25 mg. yellow  $\text{FcCH:C:CH}_2$  and 0.37 g.  $\text{FcCH}_2\text{C:CH}$  which was readily oxidized to  $\text{FcCOC:CH}$ . XIV gave in a similar run the same products. XI (0.37 g.) treated 15 min. with  $\text{NaNH}_2$  in liquid  $\text{NH}_3$  yielded 48 mg.  $\text{FcCH:C:CHMe}$ , 37 mg. XVI, and 14 mg. III ( $n = 2$ ) (XIX). Better yields of XIX and two additional compounds were obtained in runs with increased reaction times. IV (0.21 g.) in 4 cc. dry  $\text{Et}_2\text{O}$  added dropwise with stirring to  $\text{NaNH}_2$  from 0.23 g. Na in liquid  $\text{NH}_3$ , stirred 1 hr., treated with 1.4 g. MeI in a little  $\text{Et}_2\text{O}$ , and stirred 0.5 hr. yielded 0.22 g.  $\text{FcC:CMe}$ , m.  $86-8^\circ$ . XX ( $R = \text{Ac}$ ) (XXI) (2 g.) treated 12 hrs. at  $20^\circ$  with 2.8 cc.  $\text{HCONMe}_2$  and 1 cc.  $\text{POCl}_3$  yielded 0.64 g. light red XX ( $R = \text{CCl:CH}_2$ ) (XXII), m.  $66-9^\circ$  (petroleum ether), and 1 g. deep violet XX ( $R = \text{CCl:CHCHO}$ ) (XXIII), m.  $88-9^\circ$  (petroleum ether); by increasing the amount of  $\text{POCl}_3$  in a similar run to 2.5 mole equivalents XXIII was obtained in yields up to  $70^\circ$ . XXII or XXIII treated 0.5 hr. with  $\text{NaNH}_2$  in liquid  $\text{NH}_3$  yielded a yellow polymer which decomposed at about  $250^\circ$ . XX ( $R = \text{PrCO}$ ) (1 g.) treated 15 min. at  $40-50^\circ$  with 0.95 cc.  $\text{HCONMe}_2$  and 0.56 cc.  $\text{POCl}_3$  gave 0.44 g. XX ( $R = \text{CCl:-CHEt}$ ) (XXIV),  $b_{0.001}$  about  $110^\circ$ , and 0.21 g. XX [ $R = \text{CCl:-C(CHO)Et}$ ] (XXV),  $b_{0.001}$  about  $135^\circ$ . XXIV (0.376 g.) treated 15 min. with  $\text{NaNH}_2$  in liquid  $\text{NH}_3$  yielded 0.12 g. XX ( $R = \text{CH:C:CHMe}$ ), m.  $82-3^\circ$  (MeOH), 0.038 g. XX ( $R = \text{CH}_2\text{CH}_2\text{C:CH}$ ), m. about  $140^\circ$  (decomposition), and a very small amount (about 5 percent) XX ( $R = \text{C:Ct}$ ). XXV gave analogous results.



222. Sonogashira, K. and Hagihara, N.,  
SYNTHESIS OF THE FERROCENE DERIVATIVES HAVING  
CONJUGATED DOUBLE BOND SYSTEMS, Kogyo Kagaku  
Zasshi, Vol. 66, No. 8, 1963, pp. 1090-1094 (In Japanese).

Fc = ferrocenyl, Q = ferrocenediyl throughout this abstract. Various ferrocene derivatives have been prepared for spectral study and oxidation potential measurements (Drefahl et al., CA 58, 13989g). Condensation of 2.6 g. FcCHO (I) and 2.6 g. p-xylylenebis (triphenylphosphonium) dichloride (II) in 15 ml. absolute EtOH in the presence of 25 ml. 0.4N LiOEtEtOH 5 hrs. at room temperature gave orange-red 200 mg. trans, trans-p-C<sub>6</sub>H<sub>4</sub> (CH:CHFc)<sub>2</sub>, m. 220° (decomposition) (C<sub>6</sub>H<sub>6</sub>), 130 mg. orange-yellow cis, cis-p-C<sub>6</sub>H<sub>4</sub> (CH:CHFc)<sub>2</sub>, m. 178-9°, and 200 mg. orange cis, trans-p-C<sub>6</sub>H<sub>4</sub> (CH:CHFc)<sub>2</sub>, m. 190° (decomposition). Similar reaction of 1.4 g. 1, 1'-diformylferrocene (III) with 2.4 g. II gave 0.9 g. purple (-QCH:CHC<sub>6</sub>H<sub>4</sub>CH:CH-p-)<sub>7</sub>, m. 83-97°, molecular weight 2400 (cryoscopic, C<sub>6</sub>H<sub>6</sub>). Reaction of 2 g. I with 3.9 g. [PhCH<sub>2</sub>PPh<sub>3</sub>]Cl (IV) gave 1.1 g. orange-red trans-FcCH:CHPh, m. 123-5°, and an orange-colored oil (presumably the cis isomer). III (0.7 g.) and 3 g. IV also gave 0.2 g. red-brown trans, trans-PhCH:CHQCH:CHPh, m. 168-70°. Refluxing 2.5 g. I with 3.7 g. 1, 4-butylenebis (triphenylphosphonium) dibromide in 20 ml. tetrahydrofuran (THF) in the presence of 10 ml. N PhLi 7 hrs. gave 10 percent trans, trans-FcCH:CHCH<sub>2</sub>CH<sub>2</sub>CH:CHFc, m. 200° (decomposition). Arbuzov reaction of (EtO)<sub>3</sub>P with ClCH<sub>2</sub>-CH:CHCH<sub>2</sub>Cl in the presence of PhNMe<sub>2</sub> under N at 130° gave 53 percent [(EtO)<sub>2</sub>P(O)CH<sub>2</sub>CH:]<sub>2</sub> (V), b<sub>15</sub> 226°. Condensation of 4 g. I and 3 g. V in 70 ml. PhMe at 120° for 8 hrs. in the presence of tert-BuOK, prepared from 1 g. K, gave 25 percent tan-red all-trans-(FcCH:CHCH:)<sub>2</sub> (VI), m. 235° (decomposition). Similarly, 2.4 g. FcCOMe and 1.7 g. V gave 0.3 g. red all-trans-(FcCMe:CHCH:)<sub>2</sub> (VII), m. 235° (decomposition), whereas 2.9 g. FcCOPh and 1.7 g. V gave 0.9 g. tan-red all-trans-(FcCPh:CHCH:)<sub>2</sub> (VIII), m. 205-20° (decomposition). Attempted preparation of VI, VII, and VIII through Wittig reaction failed. Orange-red trans, trans-(FcCH:CH)<sub>2</sub>, m. 230° (decomposition), was prepared by the reduction of 1, 4-diferrocenyl-2-butyne-1, 4-diol with LiAlH<sub>4</sub> in Et<sub>2</sub>O. Condensation of 1.1 g. I with 0.26 g. (NCCH<sub>2</sub>CH:)<sub>2</sub> in refluxing absolute EtOH in the presence of EtONa for 2 hrs. gave 65 percent red-violet all-trans-(FcCH:C(CN)CH:)<sub>2</sub>,

m. 245° (decomposition). Use of 1.5 g. III instead of I in the above gave a red-violet insoluble solid, possibly  $[-QCH:-C(CN)CH:CHC(CN):CH-]_n$ , m. 230° (decomposition), in 60 percent yield. Knoevenagel reaction of 0.3 g. I and 0.1 g.  $CH_2(CN)_2$  in a solution of piperidine in absolute EtOH gave 77 percent deep violet  $FcCH:C(CN)_2$ , m. 100-1° (petr. ether). Similarly,  $FcCOMe$  refluxed 3 hrs. with  $CH_2(CN)_2$  in absolute EtOH in the presence of  $NH_4OAc$  gave 50 percent red-violet  $FcCMe:C(CN)_2$ , m. 117-18° (petr. ether). Reaction of 2 g. I with 0.43 g.  $p-C_6H_4(NH_2)_2$  (IX) in refluxing absolute EtOH for 2 hrs. gave 80 percent brown  $p-C_6H_4(N:CHFc)_2$ , m. 250° (decomposition), while 0.5 g. III with 0.32 g. IX yielded 60 percent red-brown  $(-QCH:NC_6H_4N:CH-p-)_n$ , m. 250° (decomposition). Similarly were prepared, using benzidine, red-brown  $FcCH:NC_6H_4C_6H_4N:CHFc$ , m. 245° (decomposition), and red-brown  $(-QCH:NC_6H_4C_6H_4N:CH-)_n$ , m. 260° (decomposition), both in 90 percent yields. Ultraviolet spectra of these compounds were given and discussed.

#### F. Alcohols in Ferrocene Series

223. Barker, C. C., Hallas, G., and Thornber, M. N., FERROCENE ANALOG OF MALACHITE GREEN, Chemical Society Journal, October 1965, pp. 5759-5760.

An ether solution of *p*-dimethylaminophenyllithium, prepared from 2.8 g.  $p-BrC_6H_4NMe_2$ , was filtered under N into an ether solution of 0.85 g. Me ferrocenoate, and the mixture boiled 30 min. The addition of  $H_2O$  and removal of the solvent from the dried organic layer gave orange needles of bis (*p*-dimethylaminophenyl) ferrocenylmethanol (I), m. 155-6°. A mixture of 2.33 g. ferrocenecarboxaldehyde, 3.9 g.  $PhNMe_2$ , 30 ml. alcohol, and 26 g. 36 percent HCl boiled 20 hrs., cooled, and treated with aqueous ethanolic  $NH_3$  gave 3.1 g. deep yellow needles of bis (*p*-dimethylaminophenyl) ferrocenylmethane (II), m. 151-2°. Attempts to oxidize II to the dye with  $PbO_2$  or chloranil were unsuccessful. I was converted to the dye in HOAc. Replacement of the Ph group in Malachite green with a ferrocenyl group resulted in a hypsochromic shift of the first spectral band and a marked bathochromic shift of the second band. This effect is apparently associated with the electron donating capacity of the ferrocenyl group.

224. Dabard, R. and Gautheron, B.,  
ACTION OF FERROCENE ON CHLORIDES AND ANHYDRIDES,  
Comptes Rendus, Vol. 254, 1962, pp. 2014-2016.

Refer to item No. 154 for abstract.

225. Dormond, A., Ravoux, J. P., and Decombe, J.,  
NEW FERROCENE DERIVATIVES, Société Chimique de  
France, Bulletin, No. 3, 1966, pp. 1152-1153 (In French).

Refer to item No. 159 for abstract.

226. Falk, H. and Schlogel, K.,  
FERROCENE DERIVATIVES, XXV. FERROCENE  
ASYMMETRY, 4. THE ABSOLUTE CONFIGURATION OF  
(B- AND Y-PHENYL- $\alpha$ -OXOTETRAMETHYLENE) FERRO-  
CENE, 5. THE APPLICATION OF A SEMI-EMPIRICAL  
METHOD OF CALCULATION TO OPTICALLY ACTIVE  
FERROCENE DERIVATIVES, Monatshefte fuer Chemie,  
Vol. 96, No. 3, 1965, pp. 1065-1093 (In German) (cf. CA 62,  
16025d).

Refer to item No. 162 for abstract.

227. Furdik, M., Toma, S., Dzurilla, M., and Suchy, J.,  
FERROCENE DERIVATIVES. CONDENSATION OF  
HALOFORMS AND CHLORAL WITH SOME FERROCENE  
CARBONYL-DERIVATIVES, Chemishe Zvesti, Vol. 18,  
1964, pp. 607-613.

The aldol reaction of haloforms and chloral with ferrocenyaldehyde (I), acetylferrocene (II) and 1, 1-diacetylferrocene (III) were studied. Aldol reactions occurred only between haloforms and I to give 31.6 percent ferrocenyltrichloromethylcarbinol, brown-red, m. 150°, 15.3 percent ferrocenyltribromomethylcarbinol, yellow-brown, m. 154-6°, and 6.6 percent ferrocenyltriiodomethylcarbinol, red-brown, decomposed 240°. Reactions of haloforms with II and III did not occur, owing to steric hindrance. The reactions of chloral with II and III gave a polymeric resin, resulting from the reaction of chloral with the cyclopentadienyl nucleus.

228. Lorkowski, H. J.,  
FERROCENE DERIVATIVES. III. THE SYNTHESIS OF  
METHOXY- AND HYDROXYARYLFERROCENES, Journal  
fuer Praktische Chemie, Vol. 27, No. 1-2, 1965, pp. 6-17  
(In German) (cf. CA 60, 13269c).

Refer to item No. 174 for abstract.

229. Nesmeyanov, A. N. and Kritskaya, I. I.,  
FORMATION OF ETHERS OF FERROCENYLCARBINOLS  
AND THEIR HYDROLYSIS UNDER CONDITIONS OF ADSORP-  
TIONAL CHROMATOGRAPHY, Izvestiya Akademii Nauk  
SSSR, Seriya Khimicheskaya, No. 12, 1964, pp. 2160-2165  
(In Russian) (cf. CA 58, 7971e).

It was shown that ferrocenylcarbinols (I) can be etherified only in the presence of acid catalysts; a  $\text{SiO}_2$  surface used for chromatography is a convenient means for such etherification. Keeping the carbinol in ROH on  $\text{SiO}_2$  2 days gave the following phenylferrocenyl R ether (R shown): Me, m. 113-14°; Et, m. 55-5.5°; iso-Pr, m. 74.5-5.5°; and 1, 1'-bis ( $\alpha$ -hydroxybenzyl) ferrocene di-R ether (R shown): Me, m. 139-40°; Et, m. 106-7°. The yields were 83-98 percent. Shaking I with ROH 0.5 hr. in the presence of  $\text{SiO}_2$  was also effective. The first procedure also gave 20 percent bis (phenylferrocenyl) methyl ether, m. 142-3°; the carbinol heated with  $p\text{-MeC}_6\text{H}_4\text{SO}_2\text{Cl}$  in  $\text{C}_6\text{H}_6$  gave 84 percent, while with  $\text{KHSO}_4$ , 83.9 percent yields. When benzoylferrocene was reduced with  $\text{LiAlH}_4$  and the mixture treated with HCl, the same ether was formed in varying yields. Also formed in this reaction was  $\text{C}_{34}\text{H}_{30}\text{Fe}_2\text{O}$ , m. 111-12°, which was one of stereoisomeric forms. Benzoylferrocene was converted by a Grignard reaction into diphenylferrocenylcarbinol, m. 137-8°, which was unchanged by heating with MeOH, while with AcOH catalyst in 40 min. at room temperature 80.7 percent phenylferrocenylcarbinyl Me ether (II), m. 110.5-12°, was formed; similarly was prepared 63 percent Me diphenylferrocenylcarbinyl ether, m. 98-9°. II heated in dioxane with 50 percent AcOH 2 hrs. gave 20 percent unchanged ether, 56 percent benzoylferrocene, and some mixed stereoisomers of diphenyldiferrocenylethane, m. 204-60°. The methyl ether of methylferrocenylcarbinol under these conditions gave 66 percent methylferrocenylcarbinol, m. 74-6°, and

2.3 percent vinylferrocene, m. 48-50°. Me phenylferrocenylcarbinyl ether in 2 hrs. at 60-5° in 30 percent H<sub>2</sub>SO<sub>4</sub> gave 94.4 percent mixed isomers of diphenyldiferrocenylethane. Similarly, bis (phenylferrocenylcarbinyl) ether gave 73 percent diphenyldiferrocenylethane isomers, m. 220-60°, and some free carbinols, m. 78-80°. The ethers of ferrocenylcarbinols were also hydrolyzed in several hrs. of contact with chromatographic Al<sub>2</sub>O<sub>3</sub> in heptane.

230. Nesmeyanov, A. N., Kochetkova, N. S., Petrovskii, P. V., and Fedin, E. I.,  
PENTAETHANODIFERROCENE, Doklady Akademii Nauk SSSR, Vol. 152, No. 4, 1963, pp. 875-878 (cf. CA 53, 21856g).

The proton (nuclear) magnetic resonance spectrum of pentaethanodiferrocene (I) contains 2 peaks: a narrow one with  $31 \times 10^{-7}$  shift relative to C<sub>6</sub>H<sub>6</sub> and a wide one with a shift of  $51 \times 10^{-7}$ , with area ratio of 1:1.3. A repetition of Goldberg's work (CA 57, 1510i) showed that the same substance was formed from ferrocene and AlCl<sub>3</sub> in C<sub>6</sub>H<sub>6</sub> in the absence of (CH<sub>2</sub>Cl)<sub>2</sub>. Accordingly, the structure of I was discarded. Ferrocenyllithium and cyclopentanone gave cyclopentylferrocenylcarbinol, which dehydrated during chromatography on Al<sub>2</sub>O<sub>3</sub> into cyclopentenylferrocene, m. 65°, which gave the nuclear magnetic resonance spectrum of three peaks with shifts of  $23 \times 10^{-7}$ ,  $34 \times 10^{-7}$ , and  $52 \times 10^{-7}$ , with area ratios corresponding to 1-cyclopentenylferrocene structure and with a decided widening of the CH<sub>2</sub>-group peak, similar to that observed in the spectrum of I. The peak widening is ascribable to ring conformational changes. Treated with AlCl<sub>3</sub> in heptane, this substance gave I (probable structure given).

231. Nesmeyanov, A. N., Perevalova, E. G., Yur'eva, L. P., and Denisovich, L. I.,  
REACTION OF FERROCENECARBONITRILE WITH ORGANO-METALLIC COMPOUNDS AND THE PREPARATION OF DI- AND TRIFERROCENYLMETHYL COMPOUNDS, Izvestiya Akademii Nauk SSSR, Otdelnie Khimicheskikh Nauk SSSR, 1962, pp. 2241-2243 (cf. CA 58, 7971h).

Ferrocenecarbonitrile (I) and EtMgBr in Et<sub>2</sub>O gave after extraction of the crude product continuously with hot

petr. ether, 70 percent propionylferrocene, m. 38-9°. Similarly was prepared 79 percent acetylferrocene, m. 85-6°. Addition of BuLi in Et<sub>2</sub>O to ferrocene at room temperature, followed by addition of tetrahydrofuran, stirring 4 hrs., and addition of I gave in 12 hrs. followed by an aqueous treatment, 80 percent diferrocenyl ketone, m. 210-11°. This and ferrocenyllithium, prepared as above from BuLi, gave in 3 hrs. in Et<sub>2</sub>O, 60 percent triferrocenylcarbinol, m. 204-5° (red color on melting). This was poorly soluble in Et<sub>2</sub>O, soluble in C<sub>6</sub>H<sub>6</sub> or CCl<sub>4</sub>. On being heated or treated with Al<sub>2</sub>O<sub>3</sub> it gave an unidentified red substance. Reduction with Zn-AcOH 4 hrs. gave 59 percent triferrocenylmethane, decomposed > 200°.

232. Pauson, P. L. and Watts, W. E.,  
FERROCENE DERIVATIVES. XII. DI- AND TRIFERRO-  
CENYLMETHANE DERIVATIVES, Chemical Society Journal,  
1962, pp. 3880-3886 (cf. CA 56, 12938f).

Diferrocenylmethane is obtained from ferrocene and paraformaldehyde. Its conversion via diferrocenyl ketone into a series of diferrocenylalkanols is described.  $\alpha$ ,  $\alpha$ -Diferrocenylbenzyl alcohol can also be obtained by condensation between ferrocene and benzoylferrocene. Two routes to triferrocenylmethane and to 1, 1'-bis (ferrocenylmethyl) ferrocene, a new method for preparing ferrocenecarboxyaldehyde, and the aldol condensation of acetylferrocene are reported.

233. Reshetova, M. D., Yarysheva, L. M., Perevalova, E. G.,  
and Nesmeyanov, A. N.,  
SYNTHESIS OF SOME SUBSTITUTED FERROCENYLCAR-  
BINOLS, Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya,  
No. 12, 1965, pp. 2196-2198 (In Russian).

Chloroferrocene heated in Ac<sub>2</sub>O with 85 percent H<sub>3</sub>PO<sub>4</sub> and P<sub>2</sub>O<sub>5</sub> 10 min. at 100° gave 1-chloro-1'-acetylferrocene, 61 percent, m. 62-3°, which with LiAlH<sub>4</sub> in Et<sub>2</sub>O gave 92 percent 1-chloro-1'- $\alpha$ -hydroxyethylferrocene, n<sub>D</sub><sup>20</sup> 1.6230; benzoate m. 70.5-71°. Similarly was prepared 88 percent 1-bromo-1'- $\alpha$ -hydroxyethylferrocene, n<sub>D</sub><sup>20</sup> 1.6375; benzoate m. 63.5-4°. 1-Acetyl-1'-cyanoferrocene and LiAlH<sub>4</sub> in Et<sub>2</sub>O gave 1-cyano-1'- $\alpha$ -hydroxyethylferrocene, 71 percent, b<sub>2.5</sub> 174-6°, 1.6260, which heated with 20 percent KOH 4 hrs.

gave 1-carboxy-1'- $\alpha$ -hydroxyethylferrocene, m. 55.5-6°. Propionylferrocene similarly gave 88 percent  $\alpha$ -hydroxypropylferrocene,  $n_D^{20}$  1.6030, which on standing changed to  $(C_5H_5FeC_5H_4CH_2Et)_2O$ , m. 86-6.5°.

234. Schlogel, K. and Falk, H.,  
THE ABSOLUTE CONFIGURATION OF 1, 2-( $\alpha$ -OXOTETRAMETHYLENE) FERROCENE, Angewandte Chemie, Vol. 76, No. 13, 1964, p. 570.

Refer to item No. 190 for abstract.

235. Sugiyama, N., Suzuki, H., Shioura, Y., and Teitei, T.,  
REACTION OF FERROCENE WITH ACYL CHLORIDES, Chemical Society of Japan Bulletin, Vol. 35, 1962, pp. 767-769.

Refer to item No. 193 for abstract.

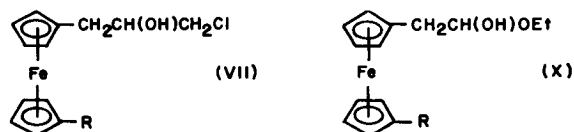
236. Ustynyuk, Y. A., Perevalova, E. G., and Nesmeyanov, A. N.,  
REACTIVITY OF COMPOUNDS CONTAINING THE FERROCENYLMETHYL GROUP COMMUNICATION 8. WITTIG REARRANGEMENT OF FERROCENYLMETHYL ETHERS, Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 1, January 1964, pp. 70-73.

The Wittig rearrangement of benzylferrocenylmethyl and bis ferrocenylmethyl ethers under the action of butyllithium passes through the intermediate formation of the metalated ether and then isomerizes into the alkoxide. Metalation determines the course of reaction. The products of such reactions are carbinols. Evidence is cited that the ferrocene nucleus stabilizes an adjacent carbanionic center less powerful than the benzene nucleus.

237. Watanabe, H., Motoyama, I., and Hata, K.,  
SYNTHESIS OF GLYCIDYLFERROCENES AND RELATED COMPOUNDS, Chemical Society of Japan Bulletin, Vol. 39, No. 4, 1966, pp. 784-790.

Fc = ferrocenyl throughout this abstract. Derivatives of ferrocene (I) with 1 or 2 glycidyl substituents, useful for the formation of polymeric I derivatives, were synthesized

by the epoxidation of the corresponding chlorohydrin compounds obtained from FeLi with epichlorohydrin (II) at  $-40$  to  $-78^{\circ}$ . A small amount of ethers, formed by the reaction of the glycidyl derivatives with the solvent EtOH, were obtained under some reaction conditions in the epoxidation of the



chlorohydrins with alkali; a small amount of biferrocenyl (III) was isolated in all cases; it was presumably formed by a Wurtz-type coupling reaction of Fc radicals. I (55.8 g.) in 650 cc. Et<sub>2</sub>O treated under N at  $-20$  to  $-30^{\circ}$  with 0.6 mole BuLi in 240 cc. Et<sub>2</sub>O, warmed with stirring to room temperature over 20 hrs. and stirred 94 more hrs. at room temperature under a stream of N (150 and 250 cc. Et<sub>2</sub>O were added to replace the evaporated solvent), the resulting orange suspension treated at  $\sim -65^{\circ}$  with 138.8 g. II in 100 cc. Et<sub>2</sub>O during 2 hrs., kept 7 hrs. at  $-60^{\circ}$  or below, warmed during 16.5 hrs. to  $-40^{\circ}$  and then to room temperature, and poured into iced H<sub>2</sub>O yielded 36.8 g. crude, dark red, viscous oil; a portion distilled gave FcCH<sub>2</sub>CH(OH)Cl (IV),  $b_{0.8-0.9}$   $156-8^{\circ}$ ,  $b_{0.52-0.53}$   $144^{\circ}$ ,  $n_D^{20}$  1.6102. Crude product (9.2 g.) chromatographed on Al<sub>2</sub>O<sub>3</sub> yielded 0.03 g. I, 0.10 g. III, m.  $233.8-34.5^{\circ}$  (sealed capillary), 1.48 g. monoglycidylferrocene (V),  $n_D^{20}$  1.6093, 0.90 g. dark red, viscous diglycidylferrocene (VI),  $n_D^{20}$  1.5968,  $b_{0.09-0.12}$   $160-1^{\circ}$ , 1.80 g. IV, 1.79 g. dark red VII (R = glycidyl) (VIII),  $n_D^{20}$  1.6014, 1.89 g. VII [R = ClCH<sub>2</sub>CH(OH)CH<sub>2</sub>] (IX),  $n_D^{20}$  1.6069, and 0.10 g. mixture of compounds. A similar experiment with 2.14 moles BuLi/mole I warmed during 64 2/3 hrs. from  $-20^{\circ}$  to room temperature, and treated during 4 hrs. with 5 moles II/mole I at  $-65$  to  $-45^{\circ}$  yielded 12.8 percent V, about 0.3 percent VI, and 0.2 percent III. An experiment with 1 mole BuLi/mole I warmed during 2.75 hrs. from  $-15^{\circ}$  to room temperature and treated 3.25 hrs. at  $-70$  to  $-55^{\circ}$  with 2 moles II yielded 1.2 percent V and 0.1 percent VI. IV (0.82 g.) in 80 cc. EtOH treated at  $0-10^{\circ}$  with 5.6 g. 30 percent aqueous KOH with stirring and the mixture stirred 8 min. yielded 0.65 g. V,  $n_D^{20}$  1.6093,  $b_{0.13-0.16}$   $107-13^{\circ}$ . A similar experiment during 35 min.



gave a little X (R = H) (XI),  $n_D^{20}$  1.5796, and 87.6 percent V. IX (1.34 g.) in 16 g. EtOH treated with stirring with 15 g. 30 percent aqueous KOH and warmed during 45 min. with stirring from 10 to 25° gave 1.11 g. dark red liquid which chromatographed on  $Al_2O_3$  yielded 0.72 g. VI,  $n_D^{20}$  1.5968,  $b_{0.0-0.12}$  160-1°, 0.16 g. dark red, viscous X (R = glycidyl) (XII),  $n_D^{20}$  1.5711. A similar epoxidation during 12 min. at 0-10° increased the yield of VI to 92 percent. VIII (0.84 g.) in 8 g. EtOH treated with 4.3 g. 30 percent aqueous KOH yielded 0.58 g. VI and 0.10 g. XII. VI (1.27 g.) in 18 cc. EtOH treated 25 min. at 0-10° with 15 g. 30 percent aqueous KOH and the mixture stirred without cooling yielded 1.03 g. VI and 0.18 g. dark red XII. Crude product (16.21 g.) from I and BuLi in 141 g. EtOH stirred 10 min. with cooling with 77.5 g. 30 percent aqueous KOH, and the dark red liquid product (14.13 g.) chromatographed on  $Al_2O_3$  gave about 0.10 g. I, 80 mg. III, m. 231.0-2.0° (sealed capillary), 4.96 g. V, 1.24 g. unidentified, dark red liquid, 6.44 g. VI, and 1.12 g. mixture. The crude product from a similar run distilled gave V,  $b_{0.17-0.18}$  111-15°,  $n_D^{20}$  1.6093, and a little III.

238. Wu, H. L., Sokolova, E. B., Leites, L. A., and Petrov, A. D., SYNTHESIS AND PROPERTIES OF SECONDARY AND TERTIARY ALCOHOLS OF THE FERROCENE SERIES, Izvestiya Akademii Nauk SSSR, Otdeleniye Khimicheskikh Nauk, 1962, pp. 887-892.

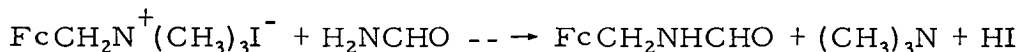
Heating  $\alpha$ -hydroxy- $\alpha$ -phenylpropylferrocene with  $KHSO_4$  at 120-50° gave only tars; heating the alcohol in vacuo at 120-50° gave 53 percent dehydration product, m. 103-4°, which was identified as  $C_{19}H_{18}Fe$ . Formylferrocene and  $RMgX$  gave: 81 percent methylferrocenylcarbinol, m. 77-8°; 98 percent phenylferrocenylcarbinol, m. 81-2°, and 91 percent benzylferrocenylcarbinol, m. 81-1.5°. Reactions with  $EtMgBr$  and  $BuMgBr$  gave not the alcohols but ethers: 48 percent bis (ferrocenylethyl) methyl ether, m. 171-1.5°, and 42 percent bis (ferrocenylbutyl) methyl ether, m. 170-1°.  $EtMgI$  gave the same result as  $EtMgBr$ . Reaction with  $CH:CHCH_2Br$  and Mg gave a polymerized product. Dehydration of the carbinols over  $Al_2O_3$  at 200° resulted in formation of bis (ferrocenylmethyl) methyl ether, m. 157°, from methylferrocenylcarbinol and vinylferrocene, obtained after dehydration by the method described by Arimoto and Haven

(CA 50, 8612h), only. Benzylferrocenylcarbinol was dehydrated either over  $\text{Al}_2\text{O}_3$  or with  $\text{KHSO}_4$  and gave 70 percent  $\beta$ -phenylvinylferrocene (I), m. 119-20°. Also described is allylferrocenylcarbinol, m. 145-7°. I and  $\text{Et}_3\text{SiH}$  in  $\text{CHCl}_3$  in the presence of  $\text{H}_2\text{PtCl}_6$  in iso-PrOH gave in 1.5 hrs. refluxing no evidence of reaction;  $\text{HSiCl}_3$  similarly treated gave only some tars.  $\text{Me}_3\text{Si}(\text{CH}_2)_3\text{Cl}$  was converted to the Grignard reagent and treated with a carbonyl derivative of ferrocene 6 hrs. at reflux in  $\text{Et}_2\text{O}$ , yielding: 75 percent ferrocenyl- $\gamma$ -trimethylsilylpropylcarbinol, m. 28°; ferrocenylmethyl- $\gamma$ -trimethylsilylpropylcarbinol, 60 percent, m. -41°; ferrocenylphenyl- $\gamma$ -trimethylsilylpropylcarbinol, 30 percent m. 98-9°.

#### G. Nitrogen Containing Ferrocene Derivatives

239. Hall, L. H. and Brown, G. M.,  
THE CRYSTAL AND MOLECULAR STRUCTURE OF  
N-FERROCENYLMETHYLFORMAMIDE,  $(\text{C}_5\text{H}_5\text{FeC}_5\text{H}_4)\text{CH}_2\text{-NHCHO}$ , Abstracts, 152 ACS Meeting, Section V, New York, September 1966.

N-Ferrocenylmethylformamide was prepared as shown in the following equation:



where "Fc" indicates the ferrocene nucleus,  $(\text{C}_5\text{H}_5\text{FeC}_5\text{H}_4)$ . The structure of this molecule is of interest because of the similarity of the oxidation-reduction characteristics of the ferrocene-ferrocenium ion couple to those of certain biological systems. In addition, the details of the structure of the ferrocene nucleus are still in some doubt because of the high thermal motion (or disorder) found in the crystal structure of unsubstituted ferrocene. Crystals of N-Ferrocenylmethylformamide obtained by recrystallization from aqueous ethanol are well-developed needles of nearly square cross-section with the axis along the needle axis. The space group is  $\text{P}2_1/\text{c}$  with  $a = 8.913 \text{ \AA}$ ,  $b = 14.333 \text{ \AA}$ ,  $c = 16.675 \text{ \AA}$ , and  $\beta = 89^\circ 11'$ . Data were collected as integrated intensities on the Oak Ridge computer-controlled x-ray diffractometer using molybdenum radiation with zirconium filtering. A

combination of theta-two theta and omega scanning techniques was used in the data collection process. The solution of the crystal structure was accomplished with the aid of the heavy atom technique. The equivalence of the carbon-carbon bonds of the cyclopentadienyl rings and the interaction of the side chain with the iron atom are discussed.

240. Hauser, C. R. and Lindsay, J. K.,  
ALKYLATIONS WITH THE METHIODIDE OF N, N-DIMETHYLAMINOMETHYLFERROCENE. SYNTHESIS OF AN  $\alpha$ -AMINO ACID HAVING THE FERROCENE GROUP, Journal of Organic Chemistry, Vol. 22, 1957, pp. 1246-1247.

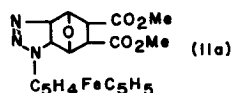
Alkylations of  $\text{NaCH}(\text{CO}_2\text{Et})_2$  (I) and  $\text{NaEt}$  acetamidocyanoacetate (II) with N, N-dimethylaminomethylferrocene-MeI (III) were effected and the products hydrolyzed and decarboxylated to form the corresponding monocarboxylic acids. The latter overall reaction produced an  $\alpha$ -amino acid having the ferrocene group which may be regarded as an analog of phenylalanine. III was prepared by the aminomethylation of ferrocene with  $\text{HCHO}$  and  $\text{NHMe}_2$ , followed by methylation of the resulting tertiary amine with MeI. I (0.1 mole) refluxed 43 hrs. with 38.5 g. III gave 34 g. of the alkylation product as an oil which slowly crystallized. This crude product (30.0 g.) refluxed 8 hrs. with 10 ml. 95 percent alcohol and 50 ml. 30 percent  $\text{KOH}$  gave 18 g. of the dicarboxylic acid,  $\text{C}_{14}\text{H}_{14}\text{O}_4\text{Fe}$  (IV), plates, m.  $133-4^\circ$  (decomposition). IV (7 g.) heated at  $145-50^\circ$  until frothing ceased (about 20 min.), the residue dissolved in N  $\text{NaOH}$ , refluxed with C, the filtrate acidified with 6N  $\text{HCl}$ , and purified gave 5 g. monocarboxylic acid,  $\text{C}_{13}\text{H}_{14}\text{O}_2\text{Fe}$ , needles, m.  $116-18^\circ$  (heptane). II (0.1 mole) and 0.1 mole III similarly refluxed 43 hrs. gave 30 g. of a crude alkylation product, m.  $172-8^\circ$ . Hydrolysis and decarboxylation of this product gave the amino acid,  $\text{C}_{13}\text{H}_{17}\text{O}_3\text{NFe}$  (V). Thus, 20 g. crude alkylation product refluxed 20 hrs. with 20 g.  $\text{NaOH}$  in 200 ml.  $\text{H}_2\text{O}$  and the mixture acidified with M  $\text{H}_2\text{PO}_4$  gave 13 g. V as monohydrate, plates, m.  $321-3^\circ$  (decomposition). Drying at  $110^\circ$  gave anhydrous V, m.  $321-3^\circ$  (decomposition). The Na derivative of acetonitrile failed to undergo alkylation with quaternary ammonium ion III within 1 hr. in liquid  $\text{NH}_3$  and  $\text{Et}_2\text{O}$  at  $-33^\circ$ . Since III was recovered, higher temperatures appeared to be required for such alkylations.

241. Nesmeyanov, A. N., Drozd, V. N., and Sazonova, V. A., DIAZO COMPOUNDS OF FERROCENE, Doklady Akademii Nauk SSSR, Vol. 150, No. 1, 1963, pp. 102-104 (cf. CA 52, 14579b).

Since ferrocenediazonium salts cannot be prepared with  $\text{HNO}_2$  owing to destruction of the ring by this acid, an indirect method was devised. Diazoaminoferrocene was added at  $-40^\circ$  to concentrated  $\text{HCl}$  and the mixture gradually warmed to  $-20^\circ$ , when a violet color of the diazonium salt appeared, while at  $-15^\circ$ ,  $\text{N}_2$  evolution commenced and terminated at  $-5^\circ$ ; crystals of chloroferrocene precipitated. After dilution and extraction with  $\text{Et}_2\text{O}$ , the organic extract was washed with aqueous  $\text{KOH}$  and  $\text{H}_2\text{O}$ , and evaporated yielding 72 percent chloroferrocene (I), m.  $57-8^\circ$ . The mother liquor after neutralization and extraction with  $\text{Et}_2\text{O}$  gave 62 percent ferrocenylamine, m.  $154-5^\circ$ . Similar treatment of benzenediazoaminoferrocene gave 76 percent I and traces of ferrocenylamine; similar decomposition in concentrated  $\text{HBr}$  or  $\text{HI}$  gave 70 percent bromoferrocene, m.  $32-3^\circ$ , or 72 percent iodoferrocene, m.  $42-4^\circ$ , respectively. Similar reaction with 40 percent  $\text{H}_2\text{SO}_3$  in the presence of  $\text{Et}_2\text{O}$  gave a solution containing hydroxyferrocene, which was isolated as the benzoyl derivative, m.  $108.5-9.5^\circ$ , in 30 percent yield. Benzenediazoaminoferrocene hydrolyzed as above in concentrated  $\text{HCl}$ , warmed to  $-20^\circ$  to form the diazonium salt solution, and treated with  $2\text{-C}_{10}\text{H}_7\text{OH}$  in 10 percent  $\text{KOH}$  in the cold gave, after chromatographic purification on  $\text{Al}_2\text{O}_3$ , 48 percent 1-ferrocencazo-2-naphthol (II), m.  $151-2^\circ$ , a green solid, along with 28 percent I; II gave violet solutions in organic solvents and was insoluble in alkalies. 1, 1'-Bis (benzenediazoamino) ferrocene treated similarly in the cold with concentrated  $\text{HCl}$  gave a violet solution of the bis (diazonium salt), which with  $2\text{-C}_{10}\text{H}_7\text{OH}$  as above gave a little II, 35 percent red 1-benzeneazo-2-naphthol, and 24 percent black ferrocene-1, 1'-bis (1-azo-2-naphthol), decomposing  $212-13^\circ$ .

242. Nesmeyanov, A. N., Drozd, V. N., and Sazonova, V. A., FERROCENE AZIDES, Doklady Akademii Nauk SSSR, Vol. 150, No. 2, 1963, pp. 321-324.

Bromoferrocene treated with  $\text{NaN}_3$  in aqueous  $\text{HCONMe}_2$  2 days in the dark gave 98 percent ferrocenyl azide (I), m.  $53-4^\circ$ . 1, 1'-Dibromoferrocene and  $\text{NaN}_3$  in aqueous EtOH in the presence of  $\text{Cu}_2\text{Br}_2$  gave after brief refluxing and extraction with  $\text{Et}_2\text{O}$  31 percent 1, 1'-ferrocenylenediazide (II), m.  $58.5-9.0^\circ$ , after purification on  $\text{Al}_2\text{O}_3$  in heptane. Both azides decomposed in light. Ferrocene in tetrahydrofuran (THF) was treated under N with BuLi in  $\text{Et}_2\text{O}$  5 hrs. followed by tosyl azide in  $\text{Et}_2\text{O}$  overnight; after treatment with aqueous KOH it gave 28 percent I and 6 percent II. I and  $\text{LiAlH}_4$  in  $\text{Et}_2\text{O}$  gave 72 percent ferrocenylamine, m.  $153-5^\circ$ . II gave 62 percent 1, 1'-diaminoferrrocene, yellow solid which oxidized in air; treated with  $\text{ClCO}_2\text{Et}$  in  $\text{Et}_3\text{N}-\text{C}_6\text{H}_6$  it gave after an aqueous treatment 50 percent di-Me 1, 1'-ferrocenylenedicarbamate, m.  $176-8^\circ$ . I and di-Me exo-cis-3, 6-endoxo- $\Delta^4$ -tetrahydrophthalate in EtOAc several days gave 75 percent di-Me exo-cis-4, 5-(N-ferrocenyl-triazolino)-3, 6-endoxohexahydrophthalate (IIa), decomposed  $153.5-4.0^\circ$ ,  $\text{PhMgBr}$  and I in  $\text{Et}_2\text{O}$  40 min. gave after an aqueous treatment 74 percent benzenediazoaminoferrrocene (III), decomposed  $120-2^\circ$ . Ferrocene treated with BuLi in THF- $\text{Et}_2\text{O}$  5 hrs., then treated with  $\text{PhN}_3$  at  $0^\circ$  1 hr. gave after an aqueous treatment 57 percent III and 24 percent 1, 1'-bis(benzenediazoamino) ferrocene, decomposed  $145-50^\circ$ , separated by soly. in  $\text{C}_6\text{H}_6$  and THF, respectively BuLi and ferrocene, as above, 5 hrs. at room temperature, followed by I at  $0^\circ$  0.5 hr. gave red-brown diazoaminoferrrocene, decomposed  $150-2^\circ$ .



43. Nesmeyanov, A. N., Perevalova, E. G., and Grandberg, K. I.,  
SYNTHESIS OF SOME HETEROANNULAR SUBSTITUTED  
FERROCENECARBOXYLIC ACIDS, Izvestiya Akademii Nauk  
SSSR, Seriya Khimicheskaya, No. 10, 1964, pp. 1903-1905  
(In Russian).

Refer to item No. 178 for abstract.

244. Nesmeyanov, A. N., Perevalova, E. G., and Reshetova,  
M. D.,  
N-( $\alpha$ -FERROCENYLALKYL) PYRIDINIUM SALTS, Izvestiya  
Akademii Nauk SSSR, Seriya Khimicheskaya, No. 2, 1966,  
pp. 335-337 (In Russian).

Substituted ferrocenylcarbinols treated in pyridine with  
tosyl chloride 4 hrs. gave:  $(C_5H_5FeC_5H_4CH_2N^+C_5H_5) -O_3SC_6H_4Me-p$  (I), m. 173-4°;  $(NCC_5H_4FeC_5H_4CHMeN^+C_5H_5) -O_3SC_6H_4Me-p$ , m. 139-40°. Treated with Na picrate, these gave  
the corresponding picrates: m. 131-2.5°; —;  $(C_5H_5FeC_5H_4CHMeN^+C_5H_5) -OC_6H_2(NO_2)_3-2, 4, 6$ , m. 113°. Treatment  
with KI gave the iodides:  $(C_5H_5FeC_5H_4CH_2N^+C_5H_5)I^-$ , m. 172.5-3.5°;  $(C_5H_5FeC_5H_4CHMeN^+C_5H_5)I^-$ , m. 110-12°. I  
heated with aqueous NaCN 20 min. gave 80 percent ferro-  
cynylacetonitrile, m. 79.5-80°. Similarly obtained was 69  
percent  $\alpha$ -ferrocenylpropionitrile, m. 47.5-49°. NaCN and  
N- $\alpha$ -ferrocenylbenzylpyridinium salt gave in 1 hr. at room  
temperature 45 percent ferrocenyl (phenyl) acetonitrile, m.  
124-25°. The nitriles and  $H_2O_2$  in aqueous alcohol KOH  
gave at 60°: ferrocenylacetamide, m. 164-5°;  $\alpha$ -ferrocenyl-  
propionamide, m. 116-16.5°.

245. Nesmeyanov, A. N., Perevalova, E. G., Shilovtseva, L. S.,  
and Tyurin, V. D.,  
FERROCENYLMETHYLATION BY MEANS OF N, N-  
DIMETHYLAMINOMETHYLFERROCENE AND ITS METH-  
IODIDE, Izvestiya Akademii Nauk SSSR, Otdelinie Khimi-  
cheskikh Nauk, 1962, pp. 1997-2001 (cf. CA 56, 10185a).

Heating trimethyl (ferrocenylmethyl) ammonium iodide  
(I) with aqueous  $Na_2S$  1 hr. gave 54 percent bis (ferrocenyl-  
methyl) sulfide, decomposed 107-8°, after chromatography  
on  $Al_2O_3$  and elution with petr. ether. I and NaSH in 3 hrs.  
similarly gave 33 percent bis (ferrocenylmethyl) disulfide,  
decomposed 125-7°. I and AcOH under N 12 hrs. at 95°,

followed by neutralization with dry  $\text{Na}_2\text{CO}_3$ , gave 25 percent ferrocenylmethyl acetate, m.  $74-6^\circ$ , which is rapidly hydrolyzed by aqueous  $\text{Na}_2\text{CO}_3$ ; reaction run at  $110-50^\circ$  gave an O-free substance, m.  $115-35^\circ$ , which appeared to be  $\text{C}_{12}\text{H}_{12}\text{Fe}$ . Heating  $\text{NaOAc}$  (anhydrous) with dimethyl (ferrocenylmethyl) ammonium bromide in vacuo at  $150^\circ$  5 hrs. gave 39 percent above ester, which also was formed in 89 percent yield from N, N-dimethylaminomethylferrocene (II) and  $\text{Ac}_2\text{O}$  in an ampul in 20 hrs. at  $100^\circ$ . Heating II with  $\text{MeOBz}$  under N 10 hrs. at  $130-5^\circ$  gave 50 percent ferrocenylmethyl benzoate, m.  $132-3^\circ$ ; similarly Me anthranilate gave 46 percent ferrocenylmethyl anthranilate, m.  $123-4^\circ$ . I and  $\text{EtOAc}$  in an ampul 15 hrs. at  $125^\circ$  gave 42 percent ferrocenylcarbinol Et ether,  $b_{0.3} 68-70^\circ$   $n_D^{20} 1.5840$ ;  $\text{BuOAc}$  similarly gave ferrocenylmethyl Bu ether (35 percent),  $b_2 105-6^\circ$  m.  $31.5-2.5^\circ$ ,  $n_D^{20} 1.5695$  (supercooled). I and piperidine 4 hrs. at  $110^\circ$  gave 94 percent N-(ferrocenylmethyl) piperidine, m.  $84.5-5.5^\circ$ ; II failed to react under such conditions. I and morpholine in 10 hrs. at  $130^\circ$  gave 95 percent N-(ferrocenylmethyl) morpholine, m.  $74-5^\circ$ . I and aqueous  $\text{PhNH}_2$  1.5 hrs. at reflux gave 75 percent N-(ferrocenylmethyl) aniline, m.  $84-5.5^\circ$ . I and o- $\text{C}_6\text{H}_4(\text{CO})_2\text{-NK}$  in  $\text{Me}_2\text{NCHO}$  10 hrs. at  $140^\circ$  gave 97 percent N-(ferrocenylmethyl) phthalimide, decomposed  $209-10^\circ$ , which with  $\text{N}_2\text{H}_4\text{H}_2\text{O}$  in  $\text{EtOH}$  5 hrs. at  $90^\circ$  gave ferrocenylmethylamine,  $b_{0.3} 108-10^\circ$ ,  $n_D^{20} 1.6310$ ;  $\text{HCl}$  salt decomposed  $233-5^\circ$ . Infrared spectra of the products were reported.

246. Nesmeyanov, A. N., Perevalova, E. G., Yur'eva, L. P., and Grandberg, K. I.,  
SYNTHESIS OF FERROCENE DERIVATIVES FROM NITRILES OF FERROCENECARBOXYLIC ACIDS, Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 8, 1963, pp. 1377-1380 (cf. CA 58, 7971h).

Refer to item No. 179 for abstract.

247. Nesmeyanov, A. N., Perevalova, E. G., Yur'eva, L. P., and Kakurina, L. N.,  
REACTION PRODUCTS OF CYANATION OF METHYL-  
AND ETHYLFERROCENES, Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 10, 1964, pp. 1897-1899 (In Russian).

Mixed nitriles of methylferrocenecarboxylic acids (I), formed by cyanation of methylferrocene (CA 55, 4464c) were treated, in EtOH, with 50 percent KOH and 6 percent  $H_2O_2$  1 hr. at 40-60° and gave mixed amides which were separated chromatographically on  $Al_2O_3$  into I amides as follows: 1, 2-, m. 119-20° (28 percent); 1, 3-, m. 146-7° (15 percent) and 1, 1'-isomer, m. 145-6° (13 percent). Similarly were isolated the amides of the ethyl- analog II of I: 1, 2-, m. 95-6° (8 percent); 1, 3-, m. 161-2° (14 percent), and 1, 1'-isomers, m. 141-2° (13 percent). Heating the amides with  $P_2O_5$  in MePh gave the corresponding nitriles of I: 1, 2-, m. 51-2°; 1, 3-, m. 45-6°; 1, 1'-isomers, m. 72-3°, and of II: 1, 2-, an oil; 1, 3-, an oil; 1, 1'-isomer, m. 29-30°.

248. Nesmeyanov, A. N., Sazonova, V. A., and Drozd, V. N.,  
INTRODUCTION OF AROMATIC AND HETEROCYCLIC  
RADICALS INTO FERROCENE. REACTION OF BROMO-  
FERROCENE WITH ORGANOMAGNESIUM COMPOUNDS,  
(Foreign Title Not Available), Translated into English by  
R. C. Taylor, U. S. Army Missile Command, Redstone  
Arsenal, Alabama, RSIC-573, June 1966 (Doklady Akademii  
Nauk SSSR, Vol. 165, No. 3, 1965, pp. 575-577 (In  
Russian)).

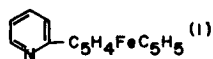
Refer to item No. 209 for abstract.

249. Nesmeyanov, A. N., Sazonova, V. A., and Gerasimenko, A. V.,  
 $\alpha$ -PYRIDYLFERROCENE AND 1, 1'-DI ( $\alpha$ -PYRIDYL)  
FERROCENE, Doklady Akademii Nauk SSSR, Vol. 147,  
1962, pp. 634-635.

Refluxing 1, 1'-ferrocenylenediboronic acid with  $CuCO_3$  in pyridine 0.5 hr. under N gave after extraction with  $Et_2O$  and evaporation of the extract a solid residue which, after chromatography on  $Al_2O_3$  and elution with heptane, followed by  $Et_2O$ , gave some ferrocene, followed by about 1 percent  $\alpha$ -pyridylferrocene (I), m. 87-9°.



Ferrocenyllithium (from BuLi in Et<sub>2</sub>O) and pyridine heated 3 hrs. under N gave after an aqueous treatment 24 percent I and a low yield of 1, 1'-di (α-pyridyl) ferrocene, m. 179-80° (in sealed tube). I gave a red solid HCl salt, which with Ph<sub>4</sub>BNa gave I tetraphenylboranate, a solid.



250. Nesmeyanov, A. N., Sazonova, V. A., and Romanenko, V. I., DIFERROCENYLAMINE, Doklady Akademii Nauk SSSR, Vol. 161, No. 5, 1965, pp. 1085-1088 (In Russian).

N-acetylferrocenylamine heated with excess EtONa 40 min. at 150° gave a red-brown Na derivative, which with bromoferrocene in the presence of CuBr 1 hr. at 110-20° gave a mixture of ferrocene, diferrocenyl, azoferrocene, starting material, and some N-acetyldiferrocenylamine, m. 176° (heptane). This and LiAlH<sub>4</sub> in Et<sub>2</sub>O 6 hrs. gave after an aqueous treatment 8.3 percent N-ethyl-diferrocenylamine, m. 149-9.5°, and yellow (70 percent) diferrocenylamine, m. 152-3° (aqueous EtOH). This and Et<sub>3</sub>O<sup>+</sup>BF<sub>4</sub><sup>-</sup> 5-10 min. at room temperature gave 56 percent ethyldiferrocenylamine, identical with the above. N-benzoylferrocenylamine in tetrahydrofuran added to LiAlH<sub>4</sub> and refluxed 6 hrs. under N gave after an aqueous treatment 86 percent benzylferrocenylamine, m. 125°; benzoyl derivative m. 134.5-5.5°. The amine and Et<sub>3</sub>O<sup>+</sup>BF<sub>4</sub><sup>-</sup> in CH<sub>2</sub>Cl<sub>2</sub> gave in 5 min. refluxing 81 percent ethylbenzylferrocenylamine, m. 48-8.5°. N-acetylferrocenylamine was reduced with LiAlH<sub>4</sub> in Et<sub>2</sub>O to 94 percent ethylferrocenylamine m. 56.5-8°, identical with the specimen formed from ferrocenylamine and Et<sub>3</sub>O<sup>+</sup>BF<sub>4</sub><sup>-</sup>.

251. Nesmeyanov, A. N., Sazonova, V. A., and Romanenko, V. I., FERROCENYLAMINE DERIVATIVES, Doklady Akademii Nauk SSSR, Vol. 157, No. 4, 1964, pp. 922-925 (cf. CA 60, 1793a).

Heating 0.06 g. Na under 2 g. Ph<sub>2</sub>NH under N at 300° until dissolved, followed by heating at 90° with 0.5 g. bromoferrocene and 1.5 g. CuBr, and finally 1 hr. at 120° gave 67 percent diphenylaminoferrocene, m. 82°. Similar reaction

of bromoferrocene with the Na derivative of AcNHPh, from EtONa and AcNHPh, at 120° 1 hr. gave a crude product, which was hydrolyzed directly with alcohol KOH to 38 percent phenylaminoferrocene, m. 69.5-70.5°; benzoyl derivative m. 177°. 1-Chloro-1-ferrocenylboronic acid heated in pyridine with Cu phthalimide 7-10 min. until a brown color developed gave 50 percent 1-chloro-1'-ferrocenylphthalimide, m. 164.5-5.5°, which heated with N<sub>2</sub>H<sub>4</sub> in EtOH 0.5 hr. gave 97 percent 1-chloro-1'-ferrocenylamine (I), m. 116°; acetyl derivative m. 124.5°. Ferrocenylamine aerated in C<sub>6</sub>H<sub>6</sub> in the presence of CuBr 15 min. gave a violet solution, which, after filtration and extraction of starting material with 10 percent HCl, gave 36 percent azoferrocene, m. 255.5°, also formed in 99 percent yield after a 4-hr. reaction period. Similar aeration of I gave 50.5 percent dichloroazoferrocene, m. 166°.

252. Nesmeyanov, A. N., Sazonova, V. A., Romanenko, V. I., Rodionova, N. A., and Zol'nikova, G. P.,  
 PHOTOLYSIS OF FERROCENE DERIVATIVES, Doklady Akademii Nauk SSSR, Vol. 155, No. 5, 1964, pp. 1130-1133.

Ferrocene metalated with BuLi, then treated with quinoline 5 hrs. on a steam bath under N gave, after an aqueous treatment, 21.6 percent  $\alpha$ -quinolylferrocene, m. 139-40°, and 6.7 percent 1, 1'-di- $\alpha$ -quinolylferrocene, m. 209°. The former gave the methiodide, an unstable violet solid. This in aqueous EtOH was kept under sunlight 1.5 hrs (or under incandescent lamp) and gave 57 percent  $\alpha$ -quinolylferrocene and 14 percent N-methyl-2-cyclopentadienylidene-1, 2-dihydroquinoline, m. 168°. Triethylferrocenylammonium iodide treated with Ag<sub>2</sub>O, filtered, and exposed to light as above gave in 4 hrs. triethylcyclopentadienylammonium ion, isolated as the tetraphenylborate, a solid precipitated by acidification of the aqueous solution. Ferrocene-1, 1'-disulfonic acid was photolyzed in aqueous solution in 6 hrs. to give 64 percent cyclopentadienylsulfonic acid as the Fe salt hexahydrate, an oil; the Fe content was determined to be Fe(II).

253. Pauson, P. L., Sandhu, M. A., and Watts, W. E.,  
FERROCENE DERIVATIVES, XV. NEW ROUTES TO  
SYMMETRICALLY DISUBSTITUTED FERROCENES, Organic  
Chemical Society Journal, No. 3, 1966, pp. 251-255  
(cf. CA 63, 11612g).

The dimethiodides of 1, 1'-bis (N, N-dimethylamino-  
methyl)- and 1, 1'-bis ( $\alpha$ -N, N-dimethylaminoethyl) ferro-  
cene have been converted into a series of symmetrically  
disubstituted ferrocenes. The direct tritylation and bis  
(aminomethylation) of ferrocene have been achieved.

254. Perevalova, E. G., Ustynyuk, Y. A., and Nesmeyanov, A. N.,  
REACTIVITY OF COMPOUNDS CONTAINING THE FERRO-  
CENYLMETHYL GROUP, COMMUNICATION 1. HYDRO-  
LYTIC CLEAVAGE OF QUATERNARY AMMONIUM SALTS,  
Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh  
Nauk, No. 6, June 1963, pp. 1036-1045.

Quaternary ammonium salts of the general formula  
 $[C_5H_5FeC_5H_4CH_2N^+(CH_3)_2CH_2R]X^-$  were prepared in high yields  
by the action of the corresponding halides on (dimethylamino-  
methyl) ferrocene in acetonitrile. These salts were then  
used in alkylation reactions, analogous to the common use  
of (ferrocenylmethyl) trimethylammonium iodide. The  
effects of the electronic properties of the  $CH_2R$  group on  
alkylation was studied using the salts' hydrolytic cleavage  
reaction as a model for comparison. The results indicate  
that the hydrolysis of quaternary ammonium salts containing  
the ferrocenylmethyl group proceeds by an  $Sn 1$  mechanism  
via the intermediate formation of a ferrocenylmethyl cation.

255. Royal College of Science and Technology, Glasgow, Scotland,  
METAL COMPLEXES OF HETEROCYCLES. I. THE  
PREPARATION OF PYRROLYL MANGANESE IRON DERI-  
VATIVES by K. K. Joshi, P. L. Pauson, A. R. Qazi, and  
W. H. Stubbs, December 1963, AD-455 501 (Unclassified  
Report) (Journal of Organometallic Chemistry, Vol. 1, 1964,  
pp. 471-475).

Reprint of research in Great Britain on preparation of  
manganese and iron derivatives of pyrrole.

256. Royal College of Science and Technology, Glasgow, Scotland,  
PREPARATION OF NOVEL ORGANOMETALLIC COMPOUNDS  
OF THE TRANSITION ELEMENTS, QUARTERLY TECHNICAL  
STATUS REPORT by P. L. Pauson, May 1964, AD-449 203,  
Contract No. DA91 591EUC3101 (Unclassified Report).

The preceding report announced the first use of a pyrrole bearing a functional substituent in the synthesis of a manganese complex. This has now been extended to the lower homologue 3-acetyl-2-methylpyrrole which affords the analogous complex and both these pyrroles were further used in the preparation of appropriately substituted azoferrocenes.

Reinvestigation of the reaction of indolylpotassium with iododicarbonylcyclopentadienyliron not only confirmed the formation of dicarbonylindolylcyclopentadienyliron, but led also to the isolation of the expected indolylcyclopentadienyliron, as an unstable oil identified spectroscopically. The structure of the dicarbonyldiallyliron described in the preceding report was thus confirmed by its synthesis from allylmagnesium chloride and iodotricarbonyldiallyliron.

257. Schlogel, K.,  
FERROCENE AMINO ACIDS, Monatshefte fuer Chemie,  
Vol. 88, 1957, pp. 601-621.

The author suggests on nomenclature ferrocenyl for  $C_5H_5FeC_5H_4-$  (abbreviated Fc-, ferrocene itself being FcH) and ferroceneyl for  $C_5H_5FeC_5H_4CO-$  (abbreviated Fc CO-). Ferrocene amino acids and some derivatives were synthesized as model substances for biologically important oxidation-reduction systems. Fc CO<sub>2</sub>H (12 g.) was suspended in 40 ml. MeOH and 60 ml. Et<sub>2</sub>O and ethereal CH<sub>2</sub>N<sub>2</sub> solution was added under cooling, whereon the precipitate dissolved under N evolution, the solvents were removed in vacuo, and the residue recrystallized from aqueous MeOH, yielding 12 g. Fc CO<sub>2</sub>Me (I), m. 70-2°. FcH was treated with PhMe-NCHO and POCl<sub>3</sub> to give 36 percent Fc CHO (II). I (9 g.) in 150 ml. absolute Et<sub>2</sub>O was reduced with 1 g. LiAlH<sub>4</sub> in 100 ml. Et<sub>2</sub>O, yielding 7.6 g. Fc CH<sub>2</sub>OH (III), m. 78-80°, after recrystallization from petroleum ether m. 79-81°. III was also obtained in 90 percent yield by LiAlH<sub>4</sub> reduction of II. To a solution of 1.73 g. III in 25 ml. dry benzene were added under ice-cooling and N, 0.2 ml. pyridine and 0.45 g. PCl<sub>3</sub> in 5 ml. benzene, the solution stirred 4 hrs. at

room temperature, diluted with benzene to 50 ml., washed with water and  $\text{NaHCO}_3$  solution, dried over  $\text{CaCl}_2$ , stirred with 2 g.  $(\text{EtO}_2\text{C})_2\text{-C}(\text{NHCOH})\text{K}$  1 hr. at room temperature, then refluxed for 5 hrs., left overnight, the solution filtered, the residue washed with benzene and  $\text{Et}_2\text{O}$ , the filtrate evaporated dissolved in ether, filtered from insoluble parts, the solution washed with water dried over  $\text{Na}_2\text{SO}_4$ , distilled at  $175\text{-}85^\circ/0.05\text{ mm.}$ , yielding 45 percent di-Et ferrocenylmethylformamidomalonate (IV), m.  $89\text{-}92^\circ$ . When III was treated with  $\text{PBr}_3$  instead of  $\text{PcL}_3$ , the benzene solution yielded 71 percent bis(ferrocenylmethyl) ether (V), m.  $134\text{-}6^\circ$  (benzene-petr. ether). To 0.8 g. IV in 15 ml. warm EtOH was added 5 ml. N NaOH, and the mixture left overnight, refluxed for 1 hr., the EtOH partially evaporated, some V filtered off, acidified with HCl, and warmed, yielding 0.45 g. N-formyl-DL-ferrocenylalanine (VI), m.  $180\text{-}5^\circ$  (decomposition) (benzene-MeOH-petr. ether). VI (0.4 g.) was boiled in 4 ml. HCl and 2 ml. AcOH under N 25 min., the solvent evaporated in vacuo, the residue dissolved in hot water, and hot saturated AcONa solution added dropwise. Cooling gave 0.3 g. DL- $\beta$ -ferrocenyl- $\alpha$ -alanine (VII), m. from  $190^\circ$ . VII (0.15 g.) and 0.08 g. KOCN were boiled in 5 ml.  $\text{H}_2\text{O}$  15 min., acidified with concentrated HCl, boiled 5 min., the solvent evaporated, the residue taken in water and filtered, and the solid recrystallized from EtOH, yielding 5-ferrocenylmethylhydantoin (VIII), m.  $217\text{-}9^\circ$  (decomposition). To 3.7 g. FcH in 30 ml.  $\text{CH}_2\text{Cl}_2$  was dropped under stirring and ice-cooling a solution of 2.67 g.  $\text{AlCl}_3$  and 2.26 g.  $\text{ClCH}_2\text{COCl}$  in 40 ml.  $\text{CH}_2\text{Cl}_2$ , the solution stirred 2 hrs. at room temperature, warmed 5 min., ice-water and HCl added, diluted with ether, the organic layer washed with water, dried over  $\text{Na}_2\text{SO}_4$ , and evaporated; the aqueous layer gave 1.2 g. FcH. Chromatography of the organic residue on  $\text{Al}_2\text{O}_3$  in benzene-petr. ether gave 0.6 g. FcH and 0.6 g. (chloroacetyl) ferrocene (IX), m.  $92\text{-}3^\circ$ . II (0.65 g.) and 0.31 g. malonic acid in 1 ml. dry pyridine were heated (water-bath) with 2 drops of piperidine for 1 hr., the solvent evaporated, the residue dissolved in EtOH, precipitated with HCl, cooled, and filtered, yielding 0.58 g. ferrocenylacrylic acid (X), m.  $183\text{-}5^\circ$  (decomposition) (aqueous EtOH). Catalytic hydrogenation of X with Pd/C gave  $\beta$ -ferrocenylpropionic acid (XI), m.  $115\text{-}18^\circ$  (benzene-petr. ether). X (0.45 g.) in 10 ml. absolute tetrahydrofuran were reduced with 0.2 g.  $\text{LiAlH}_4$  in 20 ml. ether, yielding 0.32 g. 3-ferrocenylallyl alcohol (XII), b<sub>0.05</sub>  $140\text{-}5^\circ$ , m.  $67\text{-}70^\circ$ . Reduction of XI with  $\text{LiAlH}_4$  in ether yielded 3-ferrocenylpropanol (XIII), b<sub>0.03</sub>  $135\text{-}45^\circ$ , also obtained by

catalytic hydrogenation of XII with Pd-C in EtOH. II(0.85 g.), 0.72 g. hippuric acid, and 0.35 g. NaOAc were well mixed, suspended in 1.5 ml.  $\text{Ac}_2\text{O}$ , heated for 20 min. on the water bath, cooled, stirred with EtOH and  $\text{H}_2\text{O}$ , cooled, filtered, washed with water,  $\text{NaHCO}_3$  solution, and some MeOH, yielding 0.9 g. 2-phenylferrocenylmethylene-5-oxazolone (XIV), m.  $186-9^\circ$  (EtOH-benzene-petr. ether). XIV (0.71 g.) was suspended in 2 ml. N NaOH and 4 ml. EtOH, heated on the water bath 15 min., the solution acidified hot with 2.5 ml. N HCl, and the precipitate filtered off and washed, yielding 0.71 g.  $\alpha$ -benzoylaminoferrocenylacrylic acid (XV), m.  $215-18^\circ$ . (EtOH- $\text{H}_2\text{O}$ ). XV (0.55 g.) hydrogenated with  $\text{PtO}_2$  in AcOH, yielded 0.52 g. orange N-benzoylferrocenylalanine (XVI), m.  $185-7^\circ$  (MeOH- $\text{H}_2\text{O}$ ). Acid hydrolysis of XVI gave VII, identified by paper-chromatography. Di-Et p-nitrobenzylformamidomalonate (3.4 g.) hydrogenated in 150 ml. EtOH with Raney Ni (24 hrs.), yielded 2.8 g. di-Et p-aminobenzylformamidomalonate (XVII), m.  $131-3^\circ$  (EtOH- $\text{H}_2\text{O}$ ). XVII (2.6 g.) was suspended in 12 ml. 2N HCl, diazotized with 0.6 g.  $\text{NaNO}_2$  m. ml.  $\text{H}_2\text{O}$ , the diazonium chloride solution added to a solution of 1.6 g. FcH in 50 ml. HOAc under N, stirred 5 hrs. at room temperature, 70 ml.  $\text{H}_2\text{O}$  added to the dark green solution, Zn dust added, the solution extracted with ether, the extract washed with  $\text{Na}_2\text{CO}_3$  solution water, dried over  $\text{Na}_2\text{SO}_4$ , the ether evaporated and the residue chromatographed on  $\text{Al}_2\text{O}_3$  (developer benzene-petr. ether, benzene, then ether), yielding 0.6 g. FcH and 1.66 g. di-Et p-ferrocenylphenylformamidomalonate (XVIII), m.  $162-4^\circ$ . XVIII (0.9 g.) in 8 ml. warm EtOH was treated with 4 ml. N NaOH, the precipitate dissolved after while, the solution heated 1 hr. on the water bath, the EtOH evaporated in vacuo, the aqueous solution acidified and shortly warmed, then cooled, and the precipitate filtered off and washed with water yielding 0.6 g. N-formyl-DL-p-ferrocenylphenylalanine (XIX) m.  $190-4^\circ$  (decomposition). Acid hydrolysis of XIX gave 84 percent DL-p-ferrocenylphenylalanine (XX), unmelted below  $300^\circ$  Fc $\text{CO}_2\text{H}$  (2.5 g.) in 30 ml. benzene was treated under N with 2.5 g.  $\text{PCl}_5$  at room temperature for 2 hrs., some precipitate removed, the solvents evaporated in vacuo at  $80^\circ$ , and the residue dissolved in tetrahydrofuran, giving a solution of FcCOCl (XXI). The solution of XXI was treated with the Et esters of glycine, leucine, DL-methionine, and DL-phenylalanine in tetrahydrofuran 24 hrs. at room temperature, the ester-HCl filtered off the filtrate worked up, and the residues washed with dilute HCl,  $\text{Na}_2\text{CO}_3$

solution, and water, yielding 72-93 percent of: Et N-ferrocenoylglycinate (XXII), m. 148-9°; Et N-ferrocenoyl-L-leucinate, m. 141-3°; Et N-ferrocenoyl-DL-methionate, m. 148-50°; Et N-ferrocenoyl-DL-phenylalaninate, m. 158-61°. XXI in tetrahydrofuran or I with  $\text{NH}_2\text{NH}_2 \cdot \text{H}_2\text{O}$  gave  $\text{FcCONHNH}_2$ , m. 155-8° ( $\text{CHCl}_3$ -ether). XXII (0.48 g.) in absolute ether was reduced with 0.2 g.  $\text{LiAlH}_4$  (Soxhlet principle), yielding 0.31 g. N-ferrocenylmethyl-2-aminoethanol (XXIII), m. 81-4° ( $\text{Et}_2\text{O}$ -EtOH-petr. ether). XXII was sapond. with NaOH in EtOH at room temperature, yielding 87 percent N-ferracenoylglycine (XXIV), m. 187-90° (decomposition). Similarly, N-ferrocenoylphenylalanine was obtained, monohydrate, m. about 95°. XXIV (0.29 g.), 0.11 g.  $\text{BzH}$ , 0.1 g.  $\text{NaOAc}$ , and 0.5 ml.  $\text{Ac}_2\text{O}$  heated 2 hrs. on the waterbath, treated with EtOH to induce crystallized, cooled, and the crystals filtered off gave 0.25 g. 2-ferrocenyl-4-benzyliden-5-oxazolone (XXV), m. 140-2° (MeOH). XXIV, Et L-leucinate, and excess  $(\text{C}_6\text{H}_{11}\text{N})_2\text{C}$  in  $\text{HCONMe}_2$  gave 90 percent of an oil, Et N-ferrocenoylglycyl-L-leucinate, sapond. to 67 percent N-ferrocenoylglycyl-L-leucine, m. 182-5° (decomposition). To 1.0 g.  $\text{FeCONH}_2$  in 50 ml. absolute tetrahydrofuran were added 0.4 g.  $\text{LiAlH}_4$  in 10 ml. tetrahydrofuran during 15 min., and the solution refluxed 18 hrs., yielding 0.85 g. oil, distilled (90-95° bath temperature, 0.02 mm), yielding aminomethylferrocene (XXVI), m. 30-5°; hydrochloride, m. 185-90° (EtOH). XXVI (0.43 g.) in 5 ml. absolute EtOH was heated with 0.12 g.  $\text{ClCH}_2\text{CO}_2\text{Et}$  30 min., the solvent evaporated, the residue treated with ether, the insoluble  $\text{XXVI} \cdot \text{HCl}$  removed, the ether solution distilled at 130-40°/0.02 mm; yielding 0.18 g. Et N-ferrocenylmethylglycinate, oil; hydrochloride, m. 149-51° (decomposition). XXVI (0.21 g.) in 1 ml. absolute benzene was treated with 0.2 g.  $\text{PhCH}(\text{NCO})\text{CO}_2\text{Et}$  yielding 0.39 g. N-ferrocenylmethyl-N'-( $\alpha$ -carbethoxybenzyl)urea (XXVII), m. 130-2° (benzene-petr. ether). XXVII heated in  $\text{HOAc} \cdot \text{HCl}$  for 20 min. gave 3-ferrocenylmethyl-5-phenylhydantoin, unmelted below 300° (color change). To 0.4 g.  $\text{XXVI} \cdot \text{HCl}$  suspended in 7 ml. boiling absolute toluene,  $\text{COCl}_2$  was passed in, until the solution was clear after 45 min., the solution left 30 min., the toluene removed in vacuo, the residue distilled at 110-20°/0.1 mm., yielding 0.23 g. ferrocenylmethyl isocyanate (XXVIII), orange oil. XXVIII was treated with benzylamine (1:1) yielding 82 percent N-ferrocenylmethyl-N'-benzylurea, m. 129-31° ( $\text{CH}_2\text{Cl}_2$ -petr. ether). XXVIII was shaken with a solution of Na DL-norvalinate, filtered, acidified, and the precipitate recrystallized from aqueous MeOH, yielding N-ferrocenylmethyl-N'-( $\alpha$ -carboxybutyl)urea,

m. 139-41°. FcCHO (0.22 g.), 0.14 g. KCN, and 0.5 g. (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> suspended in 10 ml. 60 percent EtOH, heated for 5 hrs. at 50-60°, for 1 hr. at 70-80°, the solution concentrated to half volume, acidified with concentrated HCl, heated for some min., cooled, filtered, and washed with water, yielded 0.2 g. 5-ferrocenylhydantoin, reprecipitated from the alk. solution with acid, recrystallized from EtOH, unmelted below 300° (color change). FcCOMe (0.9 g.), 0.2 g. NaOH, and 0.45 g. BzH in 6 ml. 50 percent aqueous EtOH were stirred 3 hrs. at room temperature, cooled in an ice-bath, and the precipitate filtered off, and recrystallized from benzene-petr. ether and then from EtOH, yielding 0.75 g. 1-ferrocenoyl-2-benzylethylene (XXIX), m. 137-40°. Catalytic hydrogenation of XXIX in EtOH with Pd-C gave 1-ferrocenoyl-2-benzylethane, m. 85-6° (petr. ether). FcCHO and PhCOMe gave similarly 76 percent 1-benzoyl-2-ferrocenylethylene, m. 138-40° (EtOH). Hydrogenation gave 1-benzoyl-2-ferrocenylethane, b<sub>0.03</sub> 150-60°. FcCHO (0.52 g.) and 0.4 g. o-hydroxyacetophenone gave similarly 0.25 g. 1-(o-hydroxybenzoyl)-2-ferrocenylethylene, m. 154-6°. Ring closure to a "flavanone" was not yet achieved. The ferrocenyl amino acids have R<sub>f</sub> values slightly higher than the corresponding phenyl amino acids.

258. Schlogel, K. and Fried, M.,  
FERROCENE DERIVATIVES. XX. FERROCENE ASYMMETRY.  
1. PREPARATION AND RESOLUTION OF ASYMMETRIC  
AMINES AND ALDEHYDES OF THE FERROCENE SERIES,  
Monatshefte, Vol. 95, No. 2, 1964, pp. 558-575 (cf. CA59,  
3325g).

Refer to item No. 191 for abstract.

259. Schlogel, K. and Fried, M.,  
SYNTHESIS OF PYRIDYL- AND QUINOLYLFERROCENES,  
Monatshefte, Vol. 94, No. 3, 1963, pp. 537-543.

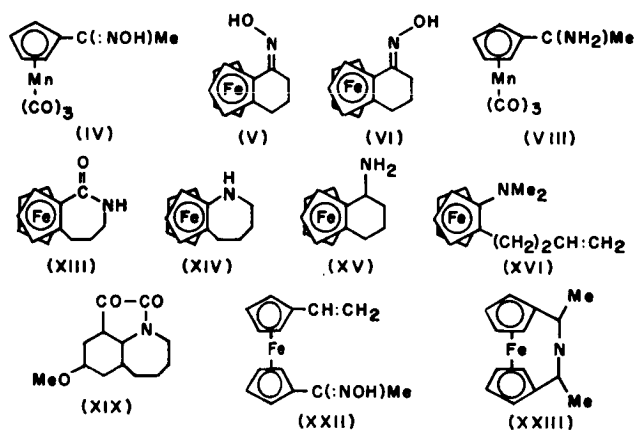
The synthesis of mono- and 1,1'-dipyridyl and -quinolyl ferrocenes is reported.  $\alpha$ -Pyridyl- and quinolyl derivatives are obtained through the Li compounds of ferrocene.  $\beta$ -Pyridylferrocenes are prepared by coupling ferrocenes with diazotized  $\beta$ -aminopyridine. Hydrogenation of both  $\alpha$ -pyridylferrocenes produces mono- or dipiperidylferrocenes. A solution of 5.60 g. ferrocene in 100 ml. absolute ether was treated under N with 46 ml. commercial solution of



BuLi in n-heptane (corresponding to 5.76 g. BuLi). The mixture was kept three days at room temperature, diluted with 50 ml. cyclohexane, treated dropwise with a solution of 4 ml. absolute pyridine in 25 ml. cyclohexane under N, excess ether distilled, the mixture refluxed 48 hrs., decomposed with H<sub>2</sub>O, and freed of resin. The organic phase was extracted with 0.1 N HCl, the acid extract alkalized with NaOH and extracted with ether to give, via chromatography on Al<sub>2</sub>O<sub>3</sub> with CH<sub>2</sub>Cl<sub>2</sub>, 2.5 g.  $\alpha$ -pyridylferrocene, m. 92-3° (petr. ether-ether), 0.3 g. red 1,1'-di- $\alpha$ -pyridylferrocene, m. 188-9° (CH<sub>2</sub>Cl<sub>2</sub>). A mixture of BuLi solution with a saturated ethereal ferrocene solution (3:1) was treated with cyclohexane and kept in the dark for about 2 weeks; deep red crystals of ferrocenyl lithium (I) separated (Li content 4.4 percent). Carboxylation of 1.82 g. I with CO<sub>2</sub> in an autoclave at 10 atmosphere yielded 1.74 g. of an acid mixture, which was separated chromatographically into 0.87 g. ferrocenecarboxylic acid and 0.80 g. ferrocene-1,1'-dicarboxylic acid. Similarly prepared from ~5 g. each of ferrocene, BuLi, and quinoline were 0.24 g.  $\alpha$ -quinolylferrocene, m. 139-41°, and 0.13 g. 1,1'-di- $\alpha$ -quinolylferrocene, m. 209-11°. A mixture of methyl( $\alpha$ -pyridyl) ferrocenes was similarly obtained; yield 0.5 g. of a yellow oil whose middle fraction (70 percent) crystallized from petr. ether, m. 37-8°, and was probably the 1- $\alpha$ -pyridyl-1'-methylferrocene. The fraction (2 percent) which migrated rapidly was 1-pyridyl-2-methylferrocene and the slow fraction (28 percent) was 1- $\alpha$ -pyridyl-3-methylferrocene. A solution of 1.88 g. 3-aminopyridine in 15 ml. H<sub>2</sub>O was treated with 7 ml. concentrated HCl (with ice-cooling) and then diazotized with 1.5 g. NaNO<sub>2</sub> in 4 ml. H<sub>2</sub>O. A solution of 1.86 g. ferrocene in 75 ml. glacial acetic acid was added. Treatment with H<sub>2</sub>O, NaOH, and then ether yielded 1.5 g. of crude product, which was separated chromatographically to give 0.4 g.  $\beta$ -pyridylferrocene, m. 57-9°, and 0.5 g. of a mixture of dipyridylferrocenes. The latter, recrystallized from benzene-petr. ether, gave a pure product, 1,1'-di- $\beta$ -pyridylferrocene, m. 141-4°. Also prepared were  $\alpha$ -piperidylferrocene [oxalate m. 212-14°(decomposed)] and 1,1'-di- $\alpha$ -piperidylferrocene; dioxalate m. 219-22° (decomposition).

260. Schlogel, K. and Mechtler, H.,  
 FERROCENE DERIVATIVES. XXVIII. REARRANGEMENT  
 OF ACRYLFERROCENE OXIMES IN THE REDUCTION WITH  
 LITHIUM ALUMINUM HYDRIDE ALUMINUM CHLORIDE,  
Monatsheft fuer Chemie, Vol. 97, No. 1, 1966, pp. 150-167  
 (In German) (cf. CA64, 5132g).

Fc = ferrocenyl throughout this abstract. The reduction of acylferrocene oximes,  $\text{FcC}(:\text{NOH})\text{R}$  (I), with  $\text{LiAlH}_4$  or  $\text{LiAlH}_4\text{-AlCl}_3$  yielded in addition to the expected  $\text{FcCH}(\text{NH}_2)\text{R}$  (II) by migration of the Fc residue also  $\text{FcNHCH}_2\text{R}$  (III). The effect of the reducing agent and of the nature of the R on the rearrangement was investigated. A tentative mechanism is proposed on the basis of the results of this investigation and of the reduction of the stereoisomeric oximes 1,2-( $\alpha$ -oxotetramethylene) ferrocene. The appropriate ketone in EtOH heated 1-3 hrs. on a water bath with two mole equivalents  $\text{NH}_2\text{OH}\cdot\text{HCl}$  and three mole equivalents  $\text{AcONa}$  yielded the corresponding I (R, percent yield, and m.p. given): Me, 88, 161-4°; Et, 79, 125-35°; Pr, 87, 111-15°; p-MeOC<sub>6</sub>H<sub>4</sub>, 48, 189-90° (decomposition);  $\alpha$ -thienyl, 70, 144-56°. Similarly prepared were the following compounds (percent yield and m.p. given): IV, 83°, 70-91°; V, —, 118-24°; VI, 75 (in mixture with V), 115-23°. The pure V or VI heated in MePh at 100° gave



from both equivalent mixtures of about equal parts V and VI. p-MeOC<sub>6</sub>H<sub>4</sub>COFc (VII) (10 g.), 10 g.  $\text{NH}_2\text{OH}\cdot\text{HCl}$ , and 40 g. KOH in 250 cc. EtOH refluxed six hours gave 3 g. unreacted VII and 3.4 g. I(R = p-MeOC<sub>6</sub>H<sub>4</sub>). The appropriate I (2.4 millimoles) in about 10 cc. tetrahydrofuran added slowly dropwise with stirring and cooling to 0.38 g.  $\text{LiAlH}_4$  in 5 cc. dry tetrahydrofuran, stirred 15 min. at room temperature,

and refluxed with stirring yielded the corresponding II and III. The results are listed in the table. Similarly prepared was VIII, oil, in less than 10 percent yield during 1 hr.; Ac derivatives, m. 101-4°. II (R = Ph) (IX) and III (R = Ph) (X) mixture in Et<sub>2</sub>O extracted with 10 percent aqueous tartaric acid gave nearly quantitative a solution of the IX in the aqueous phase and left pure X in the Et<sub>2</sub>O. All other separations were performed by treating 1 millimole amine mixture in 5 cc. dry C<sub>6</sub>H<sub>6</sub> 0.5 hr. with occasional warming with 1.5 cc. Ac<sub>2</sub>O, and chromatographing the resulting Ac derivatives.

R	Reaction Time (hrs.)	Percent Yield of		m. p. of II	m. p. of Ac Deriv.	m. p. of III	m. p. of Ac Deriv.
		II + III	II				
H	12	55	oil	147-9°	55-6°	71-3°	
Me	2	65	oil	139-41°	57-8°	-	
Et	1	64	oil	145-7°	44-6°	139-41°	
				(phenylurea deriv.)			
Pr	2	40	oil	139-40°	60-2°	-	
				(Bz deriv.)			
Ph	10	69	69-71°	208-10°	123-5°	-	
p-MeOC <sub>6</sub> H <sub>6</sub>	3	63	-	165-7°	112-14°	-	
2-thienyl	1	24	-	190-3°	92-5°	104-5°	

Ammoferrocene (XI) treated with (EtCO)<sub>2</sub>O and reducing the product with LiAlH<sub>4</sub> in boiling tetrahydrofuran gave 75 percent III (R = Pr), m. 44-6°, b<sub>0.5</sub> 110-20°. III (R = Me) (0.5 g.) in 30 cc. CHCl<sub>3</sub> refluxed under N with MnO<sub>2</sub> while adding in the beginning about 50-mg. portions MnO<sub>2</sub> at 1-hr. intervals, and the crude product treated with Ac<sub>2</sub>O yielded 50 mg. N-Ac derivative of XI, m. 170-4°. X (1 g.) in 50 cc. CHCl<sub>3</sub> refluxed 20 hrs. under N with MnO<sub>2</sub> while adding in the beginning 0.1-g. portions MnO<sub>2</sub> at 1-hr. intervals gave 0.82 g. deep red FcN:-CHPh (XII), m. 80-5°. XII (0.63 g.) in 15 cc. dioxane heated 10 min. on a water bath with 5 cc. N HCl, diluted with H<sub>2</sub>O, basified with 2N NaOH, and extracted with Et<sub>2</sub>O yielded 0.35 g. XI, m. 148-51°. XII (0.55 g.), 10 cc. 90 percent AcOH, and 2 cc. Ac<sub>2</sub>O heated 15 min. on the water bath and evaporated, and the residue chromatographed on Al<sub>2</sub>O<sub>3</sub> yielded a small amount N-Ac derivative of X and 0.3 g. N-Ac derivative of XI, m. 171-4°. X oxidized at 60-70° with K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in H<sub>2</sub>SO<sub>4</sub> gave BzOH. III (R = p-MeOC<sub>6</sub>H<sub>4</sub>) yielded similarly p-MeOC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>H, m. 183-5°. N-Ac derivative (8.3 mg.) of III (R = 2-thienyl), 4 mg. KMnO<sub>4</sub>, and 11 mg. KOH in 3.5 cc. H<sub>2</sub>O heated 3 hrs. on the water bath gave thiophene-2-carboxylic acid. V (0.1 g.), 80 mg. p-MeC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>Cl, and 60 mg. NaOH in 10 cc. 90 percent aqueous Me<sub>2</sub>CO heated 20 min. on the

water bath yielded 2 mg. XIII, m. 158-61°. V (54 mg.) in 2 cc. dry tetrahydrofuran refluxed 1.5 hrs. with stirring with 25 mg.  $\text{LiAlH}_4$  and 80 mg.  $\text{AlCl}_3$  in 4 cc. tetrahydrofuran yielded 44 mg. XIV, m. 123-6° (petroleum ether). VI remained nearly unchanged under the same conditions; only a small amount amine, presumably XV was obtained. V-VI mixture gave similarly 39 percent XIV and 35 percent unreacted VI. XIV (0.4 g.), 1.4 g. MeI, and 0.1 g.  $\text{Na}_2\text{CO}_3$  in 5 cc. MeOH heated 3 hrs. on the water bath yielded 0.5 g. XVI, m. 185-7° (decomposition). XVI (0.4 g.) and 2 cc. 10 percent KOH-MeOH evaporated and distilled gave 0.26 g. yellow-brown oily  $\alpha$ -dimethylaminobutenylferrocene (XVII), b<sub>0.005</sub> 90-5°. XVII with MeI gave an oily XVII.MeI. Oxime (2 g.) of 6-methoxy-1-tetralone reduced with 1.18 g.  $\text{LiAlH}_4$  and 3.6 g.  $\text{AlCl}_3$  in 40 cc. dry tetrahydrofuran, and the crude product dissolved in 5 cc.  $\text{Et}_2\text{O}$  and treated with saturated  $(\text{CO}_2\text{H})_2$  in  $\text{Et}_2\text{O}$  yielded 1.26 g. oxalate of 7-methoxy-1H-2,3,4,5-tetrahydro-1-benzazepine (XVIII), m. 166-71°. XVIII.  $(\text{CO}_2\text{H})_2$  (0.1 g.), 70 mg.  $\text{CCl}_3\text{CH}(\text{OH})_2$ , 90 mg.  $\text{NH}_2\text{OH} \cdot \text{HCl}$ , and 0.75 g.  $\text{Na}_2\text{SO}_4$  in  $\text{H}_2\text{O}$  refluxed 40 min. with a drop of dilute  $\text{HCl}$  and the precipitate heated 20 min. at 55° in concentrated  $\text{H}_2\text{SO}_4$  yielded 40 mg. deep red XIX, m. 134-9°; green in aqueous  $\text{NaOH}$ . Ethylferrocene acetylated and chromatographed gave the isomeric Ac derivatives which were converted to the  $\alpha$ -oxime, m. 82-8°,  $\beta$ -oxime, m. 102-12°, and 1,1'-dioxime, m. 52-65° (all from petroleum ether). The reduction of these oximes gave less than 20 percent amine mixtures; the amines were very unstable and could not be purified by chromatography. Diacetylferrocene (XX) (8.1 g.) in 100 cc.  $\text{EtOH}$ , 2.1 g.  $\text{NH}_2\text{OH} \cdot \text{HCl}$ , and 4 g.  $\text{AcONa}$  in 20 cc.  $\text{EtOH}$  refluxed 0.5 hr. yielded 1.6 g. crude monoxime (XXI), m. 139-42°. XXI reduced 3 hrs. with  $\text{LiAlH}_4$  and  $\text{AlCl}_3$  in tetrahydrofuran gave, in addition to 6 other, unidentified substances, 50 mg. mixture, m. 76-8°, of XXII and XXIII.

261. Wolf, L. and Hennig, H.,  
 COMPLEXING CAPACITY OF PYRIDOYLFERROCENOYL-  
 METHANE DERIVATIVES, Zeitschrift fuer Anorganische and  
 Allgemeine Chemie, Vol. 341, No. 1-2, 1965, pp. 1-10  
 (In German) (cf. CA61, 1489d).

Picolinoyl-, nicotinoyl-, and isonicotinoyl-ferrocenoylmethane react with direct and indirect proton donors and give characteristic pH-dependent color reactions caused by the ferrocene group.  $\text{CuCl}_2$  gives  $\text{Cu(II)}$ -diketone chelates

and mixed complexes with diketone chelate and N-salt structures. The preparation of the salts of ligand N-onium cations, their Cu(II) complexes, and the 3-pyridyl-5-ferrocenylpyrozoles is described.

262. Wyandotte Chemicals Corporation, Wyandotte, Michigan, and University of Illinois, Urbana, Illinois,  
SYNTHESIS OF METAL-CYCLOPENTADIENYL DERIVATIVES  
FOR USE AS ULTRAVIOLET ABSORBERS by R. L. Schaaf  
and K. L. Rinehart, Jr., May 1961, Report No. WADD-TR-  
61-108, AD-268 773, Contract No. AF 33(616)-7214, Project  
7312, Task 73120 (Unclassified Report).

Refer to item No. 202 for abstract.

#### H. Halogen Derivatives

263. Fish, R. W. and Rosenblum, M.,  
CONVENIENT SYNTHESIS OF SOME HALO FERROCENES,  
Journal of Organic Chemistry, Vol. 30, No. 4, 1965, pp. 1253-  
1254.

Chloromercuriferrocenes were transformed to halo ferrocenes by treatment with positive halogen reagents in polar media. Thus, N-bromo- and N-iodosuccinimide afforded bromo- and iodoferrocene, respectively. 1,1'-Dibromoferrocene (I) was similarly obtained from 1,1'-bis(chloromercuri)ferrocene. The direct conversion of ferrocene to I, without isolation of the intermediate chloromercuri derivative, was feasible.

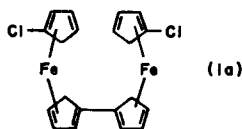
264. Hobbs, C. L., Jr.,  
DICYCLOPENTADIENYLIRON AND DICYCLOPENTADIENYL-  
NICKEL, U. S. Patent 3,092, 647 (Cl. 260-439), 4 June 1963,  
Applied 1 October 1952, 2 pp.

The anhyd. halides of Fe and Ni are treated with cyclopentadienylsodium (I) in ether or a tertiary amine to give the title compounds. Thus, 33 parts cyclopentadiene is added to a solution of Na acetylide (from 11.5 parts Na and excess  $C_2H_2$ ) in 275 parts liquid anhyd.  $NH_3$ , the mixture is refluxed at  $-32^\circ$  under N, the  $NH_3$  is replaced by dry  $Et_2O$ , and the mixture is refluxed at  $35^\circ$  for 1 hr. to give I. A solution of 28 parts anhyd.  $FeCl_3$  in dry  $Et_2O$  is added, the mixture is agitated at

room temperature 16 hrs., filtered, and the filtrate is concentrated to give 14.9 parts dicyclopentadienyliron, m. 173°, 44.1 percent yield ( $\text{FeCl}_3$ ). Similarly prepared is dicyclopentadienylnickel which sublimes at 95-8°/1.3 mm. The products can be used in the preparation of antiknock fuels.

265. Nesmeyanov, A. N., Drozd, V. N., Sazonova, V. A., Romanenko, V. I., Prof'ev, A. K., and Nikonova, L. A., DIFFEROCENYLS AND TERFERROCENYLS, Izvestiya Akademii Nauk SSSR, Otdelinie Khimicheskikh Nauk, 1963, pp. 667-674.

Treatment of hot solution of 1-(1'-chloroferrocenyl)boronic acid with ammoniacal  $\text{AgNO}_3$  gave after extn. with  $\text{Et}_2\text{O}$  and purification on  $\text{Al}_2\text{O}_3$  22 percent bis[1-(1'-chloroferrocenyl)] (Ia), m. 136.5-37°, which also formed in 88 percent yield from 1'-chloro-1-iodoferrocene and Cu in 0.5 hr. at 80-5°. Cu



and 1'-bromo-1-ethylferrocene in 0.5 hr. at 125° gave 100 percent bis[1-(1'-ethylferrocenyl)], m. 96.5-97°. Diferrocenyl stirred 2 hrs. with  $\text{AlCl}_3$  and  $\text{AcCl}$  in  $\text{CH}_2\text{Cl}_2$  gave after acidification 13.5 percent acetyldiferrocenyl, m. 137.5-8.5° and 46 percent bis[1-(1'-acetylferrocenyl)] (I), m. 187-8°. Separation on  $\text{Al}_2\text{O}_3$  by elution with  $\text{C}_6\text{H}_6$ , followed by  $\text{CHCl}_3$ - $\text{C}_6\text{H}_6$ , elution with  $\text{CHCl}_3$  gave 6.2 percent triacetyldiferrocenyl, m. 143-4°. 1'-Bromo-1-acetylferrocene and Cu in 24 hrs. at 125° gave 21.5 percent acetylferrocene and 54 percent I, m. 188-8.5°. Zn dust treated with  $\text{HgCl}_2$ -dil. HCl solution, followed by I in AcOH-concentrated. HCl and refluxed 5 min. gave 43 percent bis[1-1'-ethylferrocenyl], m. 93-4°. Me 1'-bromoferrocene-1-carboxylate and Cu in 16 hrs. at 125° gave 14 percent Me ferrocenecarboxylate and 71.5 percent bis[1-1'-carbomethoxyferrocenyl], m. 184-4.5°. Heating bromoferrocene with 1, 1'-dibromoferrocene and Cu 15 min. at 105° and 45 min. at 120° (held 0.5 hr.) gave after chromatography on  $\text{Al}_2\text{O}_3$ : ferrocene, mixed haloferrocenes, 57 percent diferrocenyl, 14 percent 1, 1'-diferrocenylferrocene, m. 212.5-14.5° (sublimed in vacuo at 240° under N), and higher polyferrocenylenes, decomposed 260-5°, after reprecipitation from  $\text{C}_6\text{H}_6$  with petroleum ether. Increased proportion of bromoferrocene in the reaction mixture gave up to 66.5 percent diferrocenyl.  $\text{BzCH}_2\text{CH}_2\text{CO}_2\text{Et}$  treated

with dry EtONa under  $C_6H_6$  15 min., followed by acetylferrocene and kept one day, gave after an aqueous treatment and heating of the aqueous layer on a steam bath 21 percent red 3-ferrocenyl-1-phenylcyclopentadiene, m.  $102-4^\circ$ , which with  $NaNH_2$  in liquid  $NH_3$  2 hrs., followed by 12 hrs. in the presence of  $FeCl_3$  in xylene, gave 22 percent 1, 1'-diferrocenyl-3, 3'-diphenylferrocene, m.  $232-3^\circ$ . This reaction in the presence of cyclopentadiene gave 77 percent ferrocene, 15 percent 1-ferrocenyl-3-phenylferrocene, m.  $172.5-73^\circ$ , and 16.5 percent 1, 1'-diferrocenyl-3, 3'-diphenylferrocene. Infrared spectra of the products were reported; the bands at 1000 and  $1113\text{ cm.}^{-1}$  were characteristic of 2 connected cyclopentadiene rings.

266. Nesmeyanov, A. N., Perevalova, E. G., and Grandberg, K. I., SYNTHESIS OF SOME HETEROANNULAR SUBSTITUTED FERROCENECARBOXYLIC ACIDS, Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 10, 1964, pp. 1903-1905 (In Russian).

Refer to item No. 178 for abstract.

267. Nesmeyanov, A. N., Perevalova, E. G., Leont'eva, L. I., and Ustynyuk, Y. A., TRIFERROCENYLCHLOROMETHANE HYDROCHLORIDE, Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, 1966, pp. 556-558 (In Russian).

Not abstracted.

268. Purdue University, Lafayette, Indiana, ALPHA-HALOFERROCENES. THE SYNTHESIS OF FERROCENYLACETYLENE by R. A. Benkeser and W. P. Fitzgerald, May 1961, Report No. AFOSR 787, AD-440 519, Contract No. AF49 635 297 (Unclassified Report) (Journal of Organic Chemistry, Vol. 26, 1961, pp. 4179-4180).

The synthesis of alpha-chloroferrocene, alphabromoethylferrocene, alpha, beta-dibromoethylferrocene, and ferrocenylacetylene are reported. The alpha-chloroethylferrocene was prepared by adding dry hydrogen chloride to vinylferrocene in pentane at  $-78^\circ C$  and recrystallization. This compound was also prepared by treating an ethereal solution of alpha-hydroxyethylferrocene containing activated alumina with anhydrous hydrogen chloride. The alpha-bromoethylferrocene

was prepared by adding anhydrous hydrogen bromide to vinylferrocene in pentane at  $-78^{\circ}\text{C}$ . Bromine was added to vinylferrocene in pentane at  $-78^{\circ}\text{C}$  to form the alpha, beta-dibromoethylferrocene. Ferrocenylacetylene was prepared by adding a solution to the dibromide in pentane to potassium amide in liquid ammonia.

269. Schlogel, K. and Steyrer, W.,  
FERROCENE DERIVATIVES, XXVII. FERROCENE ACETYLENES. 5. GENERAL METHOD FOR THE PREPARATION OF FERROCENE ACETYLENES AND FERROCENE ALLENES, Monatshefte fuer Chemie, Vol. 96, No. 5, 1945, pp. 1520-1535 (In German) (cf. CA63, 9984c).

Refer to item No. 221 for abstract.

270. Watambe, H., Motoyama, I., and Hata, K.,  
SYNTHESIS OF GLYCIDYLFERROCENES AND RELATED COMPOUNDS, Chemical Society of Japan Bulletin, Vol. 39, No. 4, 1966, pp. 784-790.

Refer to item No. 237 for abstract.



271. Frankford Arsenal, Philadelphia, Pennsylvania,  
 UNSYMMETRICAL TERTIARY PHOSPHINES OF FERROCENE  
 BY FRIEDEL-CRAFTS REACTIONS. I. FERROCENYL PHENYL-  
 PHOSPHINES by G. P. Sollott, H. E. Mertwoy, S. Portnoy, and  
 J. L. Snead, 1963, Report No. AFA A63-4, AD-416 071  
 (Unclassified Report).

Preparation of ferrocenylphenylphosphines by interaction of ferrocene with phenylphosphonous and phosphinous chlorides in presence of anhydrous aluminum chloride and representing the first unsymmetrical tertiary phosphines prepared by Friedal-Crafts process.

272. Nesmeyanov, A. N., Vil'chevskaya, V. D., Kochetkova, N. S.,  
 and Palitsyn, N. P.,  
 SYNTHESIS OF PHOSPHORUS-CONTAINING FERROCENE  
 DERIVATIVES, Izvestiya Akademii Nauk SSSR, Seriya  
Khimicheskaya, No. 11, 1963, pp. 2051-2052 (cf. Sollott and  
 Howard, CA 58, 549d).

Heating a 1:4:1 mixture of ferrocene,  $\text{PCl}_2$ , and  $\text{AlCl}_3$  3 hrs. in  $\text{CH}_2\text{Cl}_2$  followed by an aqueous treatment gave a precipitate of yellow triferrocenylphosphine oxide; an additional amount was isolated from the organic layer, total yield nearly 100 percent; crystallization from petr. ether- $\text{C}_6\text{H}_6$  gave the product,  $\text{C}_{30}\text{H}_{27}\text{Fe}_3\text{PO}$ , after removal of  $\text{C}_6\text{H}_6$  of crystallization (one molecule per two molecules phosphine oxide) at  $180^\circ$  in vacuo. The  $\text{C}_6\text{H}_6$ -free material was also obtained by crystallization from MeOH and heating in vacuo. The  $\text{C}_6\text{H}_6$ -containing product was eluted in this form from  $\text{Al}_2\text{O}_3$  by  $\text{C}_6\text{H}_6$ , while MeOH eluted the  $\text{C}_6\text{H}_6$ -free form. The oxide reacted readily with  $\text{P}_2\text{S}_5$  to give triferrocenylphosphine sulfide, purified chromatographically on  $\text{Al}_2\text{O}_3$  with  $\text{C}_6\text{H}_6$ . No further data given.

273. Pitman-Dunn Institute for Research, Frankfort Arsenal,  
 Philadelphia, Pennsylvania,  
 FERROCENYLPHOSPHONOUS DICHLORIDE FROM FERRO-  
 CENYLPHOSPHINIC ACID. THE  $\text{PH}(\text{O})\text{-P}(\text{OH})$  TAUTOMERISM  
 by G. P. Sollott and E. Howard Jr., Report No. AFA A64 18,  
 AD-450 147 (Unclassified Report).

Ferrocenylphosphinic acid is converted to ferrocenylphosphonous dichloride by reaction with a large excess of phosphorus trichloride. This is considered to be evidence that the phosphinic acid exists in tautomeric equilibrium with the phosphonous

acid form, the preparation of ferrocenylphosphonous dipiperide, the first known phosphorus amide of ferrocene, is reported.

274. Research and Development Directorate, Frankford Arsenal, Philadelphia, Pennsylvania,  
FRIEDEL-CRAFTS REACTION OF FERROCENE WITH ARSENIC TRICHLORIDE. SOME MONOFERROCENYL DERIVATIVES OF ARSENIC (III) by G. P. Sollott and W. R. Peterson, Jr., October 1964, Report No. A65-1 1C014501B13A, AD-613 655 (Unclassified Report).

The reaction of ferrocene with arsenic trichloride under Friedel-Crafts conditions has been found to give only mono-substitution on arsenic. Results of efforts to optimize the yield of arsenosoferrocene thus obtained are presented. Arsenosoferrocene, formulated as a dimer, is readily converted to ferrocenyldichloroarsine, oxybis (ferrocenylchloroarsine), a polymeric arsenosoferrocene, and arsenoferrocene. The compounds described are the first known arsenic-containing ferrocene derivatives. The bis (chloroarsine) appears to be the first example of a new class of compounds of the type (RASCL) 20.

Varied behavior encountered when dimeric arsenosoferrocene is converted to the polymeric species in aqueous alkali is explained in terms of hydrolysis of the ferrocene-arsonite anion. Conversion of the dimer to the polymer in various solvents is attributed to solvolysis of the arsenic-oxygen linkage.

Adsorptions shown by ferrocene and benzene derivatives in the region, 750-700/cm. are associated with AS-O-AS bridges. Ferrocene is less reactive than benzene in Friedel-Crafts reactions with acid chlorides of ASIII, although more reactive with acid chlorides of PIIL. A possible explanation for this anomalous behavior is suggested.

275. Sollott, G. P.,  
STUDIES IN THE SYNTHESIS OF PHOSPHORUS-CONTAINING FERROCENE DERIVATIVES, University Microfilms, (Ann Arbor, Michigan) Order No. 62-2668, 123 pp., Dissertation Abstract, Vol. 23, 1962, pp. 447-448.

The preparation of the first known compounds with phosphorus bonded to ferrocene carbon is described. The reaction of ferrocene with phosphorus trichloride in the presence of anhydrous aluminum chloride under conditions favoring

monosubstitution gave rise to three products: ferrocenylphosphonous dichloride, diferrocenylphosphinous chloride and triferrocenylphosphine. Formation of these compounds was demonstrated when the following derivatives were isolated: 1) Ferrocenylphosphinic acid, 2) Diferrocenylphosphinic acid and its hydrate, 3) Triferrocenylphosphine oxide, several of its hydrates and a hydrogen chloride complex, and 4) Triferrocenylmethylphosphonium iodide. A tertiary phosphine was thus observed among the products of a Friedel-Crafts reaction for the first time.

The method for converting primary phosphinic acids to phosphonous dichlorides by reaction with a large excess of phosphorus trichloride was shown to apply to ferrocenylphosphinic acid. Ferrocenylphosphonous dichloride thus formed was converted by reaction with piperidine to ferrocenylphosphonous dipiperidide.

The reaction of a mixture of mono- and dilithioferrocenes with excess phosphorus oxychloride led to the formation of ferrocenylphosphonic dichloride. This was demonstrated when ferrocenylphosphonic acid and its hydrate were isolated. Efforts to prepare triferrocenylphosphine by the reaction of phosphorus trichloride with lithioferrocenes were unsuccessful.

Infrared absorption bands were assigned to the ferrocenylphosphorus group. The possible existence of an interaction between phosphoryl and the ferrocene residues in anhydrous triferrocenylphosphine oxide in the solid state is discussed. Infrared spectral evidence for ring hydration, ring hydrochlorination, and for hydrogen-bonding of P-O-H to the ring  $\pi$  electrons is presented, and an absorption band assigned to hydrogen-bonding of the ring  $\pi$  electrons (i. e., ring complexing).

A study of electronic spectra indicated that there is little electronic interaction of pentavalent phosphorus with attached ferrocenyl groups.

276. Sollott, G. P. and Howard, E., Jr.,  
FRIEDEL-CRAFTS REACTION OF FERROCENE WITH PHOSPHORUS TRICHLORIDE. FORMATION OF TRIFERROCENYLPHOSPHINE, Journal of Organic Chemistry, Vol. 27, 1962, pp. 4034-4040 (Frankford Arsenal, Pitman Dunn Laboratories, Philadelphia, Pennsylvania, Report No. A62-15, N63-13327).

The preparation of the first known compounds with phosphorus bonded to ferrocene carbon is described. The reaction of ferrocene with phosphorus trichloride in the presence of anhydrous aluminum chloride under conditions favoring

monosubstitution gave rise to three products: 1) Ferrocenylphosphonous dichloride, 2) Differocenylphosphinous chloride, and 3) Triferrocenylphosphine. Formation of these compounds was demonstrated when the following derivatives were isolated: 1) Ferrocenylphosphinic acid; 2) Differocenylphosphinic acid and its hydrate; 3) Triferrocenylphosphine oxide, several of its hydrates, and a hydrogen chloride complex and 4) Triferrocenylmethylphosphonium iodide. A tertiary phosphine was thus observed among the products of a Friedel-Crafts reaction for the first time. Infrared absorption bands were assigned to the ferrocenyl-phosphorus group. The possible existence of an interaction between phosphoryl and the ferrocene residues in the anhydr. phosphine oxide is discussed. Spectral evidence for ring hydration and ring hydrochlorination is presented.

277. Sollott, G. P., Mertwoy, H. E., Portnoy, S., and Snead, J. L., UNSYMMETRICAL TERTIARY PHOSPHINES OF FERROCENE BY FRIEDEL-CRAFTS REACTIONS. I. FERROCENYLPHENYLPHOSPHINES, Journal of Organic Chemistry, Vol. 28, 1963, pp. 1090-1092.

Ferrocenylphenylphosphines have been prepared in good yield by the interaction of ferrocene with phenylphosphonous and -phosphinous chlorides in the presence of anhydrous  $\text{AlCl}_3$ , and represent the first unsymmetrical tertiary phosphines prepared by a Friedel-Crafts process. The air-stable phosphines were also obtained as the oxides and methiodides, the former directly from the reaction mixtures. The mechanism of Friedel-Crafts trisubstitution on phosphorus is discussed.

278. Sollott, G. P. and Peterson, W. R., Jr., TRIFERROCENYLPHOSPHINE AND DIFERROCENYLPHOSPHINOUS CHLORIDE. NOVEL PREPARATION AND CHARACTERIZATION, Journal of Organometallic Chemistry, Vol. 4, No. 6, 1965, pp. 491-493

The preparation of triferrocenylphosphine oxide (I) in 78 percent yield reported by Nesmeyanov, et al. (CA 60, 5548g) could not be repeated by the present authors. To 0.05 mole  $\text{H}_2\text{NPCl}_2$  in 100 ml. heptane under  $\text{N}_2$  was added dropwise 0.15 mole each of ferrocene and  $\text{AlCl}_3$  in 250 ml. heptane, the whole stirred and refluxed 20 hrs., treated with 500 ml.  $\text{H}_2\text{O}$ , extracted with  $\text{C}_6\text{H}_6$ , and the combined extracts concentrated and separated by chromatography on a 100-cm. column of activated  $\text{Al}_2\text{O}_3$ . Elution with  $\text{C}_6\text{H}_6$  gave triferrocenylphosphine

(II), m. 271-3° (sealed capillary) (heptane); elution with  $\text{CHCl}_3$  gave I. II in  $\text{C}_6\text{H}_6$  at room temperature with air was stable; at the b. p. with air, II was partially converted to I. II and S in  $\text{C}_6\text{H}_6$  gave 100 percent sulfide, m. 291-3° (decomposed) ( $\text{C}_6\text{H}_6$ ); II and Se gave 100 percent selenide, m. 297-9° (decomposition) ( $\text{C}_6\text{H}_6$ ). The reaction of  $\text{Et}_2\text{NPCl}_2$ ,  $\text{AlCl}_3$ , and ferrocene as above gave yields of 5 percent  $(\text{C}_5\text{H}_5)_2\text{FePCl}_2$ , 9 percent  $[(\text{C}_5\text{H}_5)_2\text{Fe}]_2\text{PNEt}_2$ , m. 134.0-6.5°. III and  $\text{PhMgBr}$  gave  $[(\text{C}_5\text{H}_5)_2\text{Fe}]_2\text{PPh}$ ; III and  $\text{H}_2\text{O}$  gave the oxide, m. 190-3° (decomposition) ( $\text{C}_6\text{H}_6$ -heptane); and III and aqueous  $\text{NaOH}$  gave mostly  $[(\text{C}_5\text{H}_5)_2\text{Fe}]_2\text{PHO}$ .

279. Sollott, G. P., Snead, J. L., Portnoy, S., Peterson, W. R., Jr., and Mertwoy, H. E.,  
 PHOSPHORUS, ARSENIC, AND BORON-CONTAINING FERROCENE DERIVATIVES, Army Science Conference Proceedings, Vol II, 1965, pp. 441-452 (N65-22309, N65-22275 12-34).

The preparation of diferrocenyl-phenylphosphines by reactions of p-methoxy-, p-methyl-, p-chloro-, and p-cyano-phenylphosphonous dichlorides with ferrocene under Friedel-Crafts conditions was reported. Also, ferrocene was found to react with arsenic trichloride in the presence of anhydrous  $\text{AlCl}_3$  to give only monosubstitution on arsenic. Further, ferrocenylarsenic oxide was converted to ferrocenyldichloroarsine and bis-ferrocenylchloroarsenic and bis-ferrocenylhydroxyarsenic oxides. Ferrocenylboronic acid was prepared by the reaction of ferrocene with  $\text{BCl}_3$ , and the boronic acid was converted to ferrocenylboronic anhydride trimer. The preparation of 1,1'-bis-diphenylphosphino ferrocene and ferrocenyldiphenylphosphine, and their arsenic analogs by reactions with mixtures of mono- and di-lithioferrocenes was also announced.

## J. Organometallic Ferrocene Derivatives

280. California University, Department of Chemistry, Riverside, California,  
CARBAMETALLIC BORON HYDRIDE DERIVATIVES. I. APPARENT ANALOGS OF FERROCENE AND FERRICINIUM ION by M. F. Hawthorne, D. C. Young, and P. A. Wegner, February 1965, Report No. AROD 3763 10, AD-624 390, Contract No. DA ARO(D)-31-124-G547 (Unclassified Report).

The synthesis of very stable ionic species is reported which exhibit many of the properties of pi-bonded organometallic compounds and which may contain a single Fe (II-III) simultaneously bonded to the open faces of two  $B_9C_2H_{11}(-2)$  Icosahedral fragments. Chemical Evidence suggests that each  $B_9C_2H_{11}(-2)$  unit contributes six electrons for bonding to Fe (+2) in  $Fe(B_9C_2H_{11})_2(-2)$  and the two  $B_9C_2H_{11}(-2)$  units complete the krypton shell about iron. The novel "sandwich" structure which would allow a single iron atom to complete two carborane icosahedra cannot be ruled out with the evidence at hand.

281. Dynamics Corporation of America, Mingham, Massachusetts, STUDIES IN ORGANOMETALLIC CHEMISTRY by D. Seyferth, August 1962, Report No. NONR134143, AD-283 933 (Unclassified Report).

Contents: Vinyl compounds of metals, Hydroboration of trimethylvinylsilane silicon- and tin-substituted boranes and their oxidation oxymercuration of trimethylvinylsilane vinyl-lithium preparation and cleavage of perfluorovinyltin compounds organogermanium chemistry, Tri ethyl(iso)cyanogermane trimethyl(iso)cyanogermane-iron tetracarbonyl triphenylgermyl-substituted ferrocens and related compounds trimethylgermylbenzene chromium tricarbonyl the triphenylgermyltriphenylborate anion lithium trimethylsilanolate and lithium trimethylgermanolate.

282. Dynamics Corporation of America, Mingham, Massachusetts, THE PREPARATION OF ORGANOLITHIUM COMPOUNDS BY THE TRANSMETALATION REACTION. II. FERROCENYL-LITHIUM by D. Seyferth and J. F. Helling, June 1961, Report No. NONR184143, AD-259 319.(Unclassified Report).

The synthesis of ferrocenyllithium was undertaken by the transmetalation reaction using ferrocenylmercuric chloride (I)

as the starting material. The reaction of I with phenyllithium in ether solution, followed by carbonation gave ferrocenecarboxylic acid and benzoic acid. Similar results were obtained in ether-tetrahydrofuran mixtures. The transmetalation went practically to completion when ethyllithium was used in place of phenyllithium. In another experiment, I and ethyllithium (1:2.5 mol-ratio) were mixed, and solid triphenylchlorosilane was added after one hr. Ferrocenyltriphenylsilane was isolated in 66 percent yield as well as ferrocene in 8 percent yield. Evidence of some dilithiated product was found when the I-ethyllithium reaction mixture was treated with benzophenone.

283. Dynamics Corporation of America, Mingham, Massachusetts, TRIPHENYLGERMYL-SUBSTITUTED FERROCENES. NEW SYNTHESSES OF FERROCENYL LITHIUM AND GRIGNARD REAGENTS by D. Seyferth and H. P. Hofmann, October 1961, Report No. NONR184143, AD-264 343 (Unclassified Report).

Reactions, Substitution Reactions, Sodium Compounds, Mercury Compounds. Treatment of the disodioferrocene with magnesium bromide in ether represents a new route to the ferrocene di-grignard reagents addition of triphenylbromogermane to the di-grignard solution resulted in almost none of the disubstituted product, but a 32 percent yield of triphenylgermylferrocene was realized. A new preparation of ferrocenyllithium and 1,1'-ferrocenylenedilithium by the transmetalation reaction occurring between ethyllithium and the corresponding chloromercuriferrocenes in ether is described. The reaction of 1,1'-ferrocenylenedilithium with trimethylchlorosilane produced significant amounts of the monosubstituted product in addition to 1,1'-bis(trimethylsilyl)ferrocene. The preparation of 1,1'-bis(triphenylgermyl)titanocene dichloride, triphenylgermylmanganese pentacarbonyl and triphenylgermyl-pi-cyclopentadienyliron dicarbonyl is described.

284. Goldberg, S.I., Keith, L. H., and Prokopov, T. S., A CONVENIENT PREPARATION OF MONOLITHIOFERROCENE, Journal of Organic Chemistry, Vol. 28, 1963, pp. 850-851.

A monolithiation technique was outlined which would provide monolithioferrocene in the absence of dilithioferrocene. Ferrocene (10 g.) in 150 ml. Et<sub>2</sub>O was treated under a N atmosphere with 35 ml. 1.59 M BuLi and the mixture stirred six hrs. at room temperature. A five ml. aliquot was removed and added to dry ice and Et<sub>2</sub>O, evaporated washed, the combined aqueous

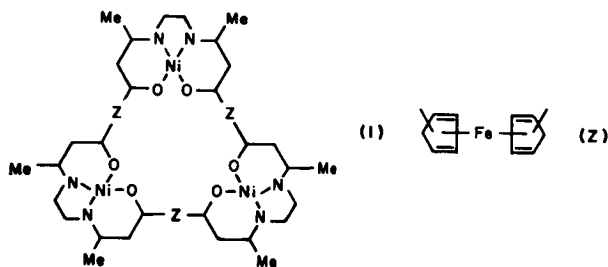
extracts acidified, and the precipitate collected and found to be soluble in  $\text{Et}_2\text{O}$  giving no indication of the ferrocenedicarboxylic acid. The solution was dried, evaporated, and 25 percent ferrocenecarboxylic acid (I) obtained. In other runs, carbonation was carried out after 4.5 and eight hrs. of lithiation. In each case only I was obtained in yields of 20, 26, and 21 percent, respectively.

285. Hawthorne, M. F. and Pilling, R. L.,  
 CARBAMETALLIC BORON HYDRIDE DERIVATIVES. III.  
 THE  $\pi\text{-C}_5\text{H}_5\text{Fe}(\pi\text{-B}_9\text{C}_2\text{H}_{11})$  SYSTEM, American Chemical Society Journal, Vol. 87, 1965, p. 3987.

The preparation of  $\pi\text{-C}_5\text{H}_5\text{Fe}(\pi\text{-B}_9\text{C}_2\text{H}_{11})$  containing  $\text{Fe}^{\text{II}}$  and  $\text{Fe}^{\text{III}}$  is described. Accompanying communication describes single crystal X-ray diffraction which confirms the "sandwich" structure.

286. Olszewski, E. J. and Martin, D. F.,  
 TEMPLATE SYNTHESIS OF A NOVEL BIMETALLIC FERROCENE-SCHIFF BASE COMPLEX, Journal of Organometallic Chemistry, Vol. 5, No. 2, 1966, pp. 203-204.

A novel type of organometallic-metal-chelate compound was prepared by means of a template system. Thus, interaction of a ferrocenebis( $\beta$ -diketone), 1,1'-(1,3-butanedione)-ferrocene and a nickel (II) template [ $\mu$ -dichlorotetrakisethylene diaminedi-nickel(II) chloride plus pyridine] affords the condensation



product I. The product was obtained in a highly pure state.

287. Perevalova, E. G., Ustynyuk, Y. A., and Nesmeyanov, A. N.,  
 REACTIVITY OF COMPOUNDS CONTAINING THE FERROCENYLMETHYL GROUP, Izvestiya Akademii Nauk SSSR, Seriya Kimicheskaya, No. 11, November 1963, pp. 1972-1977.

The cleavage of benzyl ferrocenylmethyl ether, ferrocenylmethyl furfuryl ether, bisferrocenylmethyl ether,



1-ferrocenylethylmethyl ether, and  $\alpha$ -ferrocenylbenzylmethyl ether by lithium in THF was found to give ferrocenylmethyl lithium except in the case of ferrocenylmethyl furfuryl ether where methyl ferrocene was obtained.

288. Purdue University, Lafayette, Indiana,  
THE METALATION OF DIPHENYLFERROCENYLCARBINOL  
by R. A. Benkeser, W. P. Fitzgerald and M. S. Melzer,  
Report No. AFOSR TN60 1365, AD-246 801, Contract No.  
AF49 638 297 (Unclassified Report).

Preparation of organometallics.

289. Rausch, M. D.,  
FERROCENE AND RELATED ORGANOMETALLIC  $\pi$ -COM-  
PLEXES. VI. THERMAL DECOMPOSITION OF DIFERRO-  
CENYLMERCURY, Inorganic Chemistry, Vol. 1, 1962,  
pp. 414-417 (cf. CA 55, 23473e; 56, 8741i).

Thermal decomposition of diferrocenylmercury,  $(\text{FeC}_{10}\text{H}_9)_2\text{Hg}$ , produced biferrocenyl in yields of 30-61 percent in the presence of Ag. The results suggested a homolytic mechanism of decomposition involving ferrocenyl radicals and ferrocenylene diradicals. Simultaneous decomposition of  $(\text{FeC}_{10}\text{H}_9)_2\text{Hg}$  and other diaryl Hg compounds in the presence of Ag provided a new synthesis of arylferrocenes. Reaction of  $(\text{FeC}_{10}\text{H}_9)_2\text{Hg}$  with BuLi in excess produced monolithioferrocene.

290. Royal Aircraft Establishment, Farnborough, England,  
FERROCENE POLYMERS. PART III. SOME ASPECTS OF THE  
REACTION BETWEEN FERROCENE AND PHENYLSODIUM  
by W. A. Lee and J. S. Pippett, AD-286 417 (Unclassified  
Report).

The reaction of ferrocene with amylsodium and phenylsodium is discussed. Some effects of the method of preparation and purity of the phenylsodium, and of the time and temperature variations on the metalation of ferrocene are reported. A reliable procedure for the synthesis of pure 1,1'-disodioferrocene free from monosodiocompounds was not found; some decomposition of the ferrocene moiety appears to occur during the reaction. The main product from a room-temperature reaction appears to be monosodioferrocene. The mixture of ferrocene and phenylsodium must be stored at room temperature before heating, to avoid very low yields of 1,1'-disodioferrocene.

and high yields of by-products. Recommendations for further work are outlined.

291. Seyferth, D., Hoffmann, H. P., Burton, R. and Helling, J. F., TRIPHENYLGERMYL-SUBSTITUTED FERROCENES AND RELATED COMPOUNDS. NEW SYNTHESIS OF FERROCENYL-LITHIUM AND GRIGNARD REAGENTS, Inorganic Chemistry, Vol. 1, 1962, pp. 227-231 (cf. Nesmeyanov, et al., CA 53, 1293d).

1,1-Ferrocenylenedisodium (I) and  $\text{Ph}_3\text{GeBr}$  gave 53-77 percent hexaphenyldigermoxane, 12-13 percent 1,1'-bis(triphenylgermyl)ferrocene, and 4-10 percent triphenylgermylferrocene. Similar behavior was observed with  $\text{Me}_3\text{SiCl}$ . 1,1'-Ferrocylenebis(magnesium bromide) (II) was prepared by stirring for one hr. a mixture of 1,1'-ferrocenylenedisodium in 250 ml.  $\text{Et}_2\text{O}$  and anhydrous  $\text{MgBr}_2$ , prepared from 0.057 mole  $(\text{BrCH}_2)_2$  and 0.057 g.-atom Mg. The ferrocenylenedisodium was prepared from 0.028 mole ferrocene and n-amyl sodium in pentane. II gave 1,1'-ferrocenedicarboxylic acid with  $\text{CO}_2$  but a 32 percent yield of triphenylgermylferrocene with  $\text{Ph}_3\text{GeBr}$  and almost no disubstituted product. Ferrocenyllithium (III) was prepared from 4.2 millimoles chromomercuriferrocene in a Schlenk tube, evacuated, and filled with argon, 9 ml.  $\text{Et}_2\text{O}$  and 9.3 millimoles  $\text{EtLi}$  in  $\text{Et}_2\text{O}$  added in succession at  $27^\circ$ , and the mixture stirred 45 min. The preparation of 1,1'-bis(triphenylgermyl)titanocene dichloride, triphenylgermylmanganese pentacarbonyl, and triphenylgermyl- $\pi$ -cyclopentadienyliron dicarbonyl are described.

292. Wolf, L. and Hennig, H., COMPLEXING CAPACITY OF PYRIDOYLFERROCENOYL-METHANE DERIVATIVES, Zeitschrift fur Anorganische und Allgemeine Chemie, Vol. 341, No. 1-2, 1965, pp. 1-10 (In German) (cf. CA 61, 1489d).

Picolinoyl-, nicotinoyl-, and isonicotinoylferrocenoylmethane react with direct and indirect proton donors and give characteristic pH-dependent color reactions caused by the ferrocene group.  $\text{CuCl}_2$  gives Cu(II)-diketone chelates and mixed complexes with diketone chelate and N-salt structures. The preparation of the salts of ligand N-onium cations, their Cu(II) complexes, and the 3-pyridyl-5-ferrocenylpyrazoles is described.

293. Bublitz, D. E. and Harris, G. H.,  
THE PREPARATION AND PROPERTIES OF METALLOCENE-  
THIOLCARBOXYLATE ESTERS, Journal of Organometallic  
Chemistry, Vol. 4, No. 5, 1965, pp. 404-408.

Ferrocene, ruthenocene, and cyclopentadienylmanganese tricarbonyl have been shown to undergo either alkylation or conversion to thiolcarboxylate esters when treated with substituted chlorothiolformates in the presence of aluminum chloride. While aryl or primary alkyl chlorothiolformates provide the corresponding thiol esters, tert-butyl chlorothiolformate gives only alkylation products derived from the tert-butyl cation. Competitive alkylation and acylation reactions occur when isopropyl chlorothiolformate is used. Methyl ferrocenethiolcarboxylate, prepared by this method, has been converted via displacement reactions to ferrocenoic acid, its hydrazide, and several amide derivatives.

294. Drozd, V. N., Sazonova, V. A., and Nesmeyanov, A. N.,  
FERROCENYL SULFONES. FERROCENYL MESITYL  
SULFONE UNDER THE CONDITIONS OF THE SMILES  
REARRANGEMENT, Doklady Akademii Nauk SSSR, Vol.  
159, No. 3, 1964, pp. 591-594 (In Russian).

Keeping 0.9 g. bromoferrocene with 1.6 g. Cu benzenesulfinate in  $\text{Me}_2\text{NCHO}$  two days gave, after an aqueous treatment, 82 percent Ph ferrocenyl sulfone, m. 153.5-54°; the yield was 78 percent after heating the mixture on a steam bath. Similarly, Cu ferrocenesulfinate gave 85 percent diferrocenyl sulfone, decomposed 270-3°, also formed in low yield from Cu ferrocenesulfinate kept alone in  $\text{Ph}_2\text{NCHO}$  two days. Bromoferrocene and Cu mesitylenesulfinate in  $\text{Me}_2\text{NCHO}$  two days gave seven percent mesityl ferrocenyl sulfone m. 148-9°. Thiomesitylene was converted to the Cu salt and this with bromoferrocene in 40 min. at 130° gave 86 percent mesityl ferrocenyl sulfide, m. 85.5-6.5°, which with  $\text{H}_2\text{O}_2$  in  $\text{MeOH-KOH}$  at pH 7 to 9 in 25 hrs. gave 62 percent mesityl ferrocenyl sulfone (I) and 21 percent mesityl ferrocenyl sulfoxide, m. 126-7°. I and BuLi in  $\text{Et}_2\text{O}$  overnight gave Li ferrocenesulfinate.

295. Egger, H. and Schlogel, K.,  
FERROCENE DERIVATIVES. XXIII. FERROCENYLACETYLENES. 4. PREPARATION AND LIGHT-ABSORPTION OF FERROCENYLTHIOPHENES AND FERROCENYLACETYLENES, Monatshefte Chemie, Vol. 95, No. 6, 1964, pp. 1750-1758 (In German) (Cf. CA 59, 7557f; 61, 14708h, 16091g).

Refer to item No. 213 for abstract.

296. Knox, G. R. and Pauson, P. L.,  
FERROCENE DERIVATIVES - SOME SULFUR COMPOUNDS, Journal of Chemical Society, 1958, pp. 692-696.

Ferrocenesulfonic acid (I) was obtained by an improved method and converted via the sulfonyl chloride (II) into ferrocenethiol (III), characterized as its S-Me (IV) and S-allyl ether (V), as its S-HO<sub>2</sub>CCH<sub>2</sub> (VI) and S-Ac derivative (VII) and as the corresponding disulfide (VIII). Ferrocene (IX) (8 g.) in 60 ml. Ac<sub>2</sub>O treated during 10 min. at 23° with five g. tech. ClSO<sub>3</sub>H (X) gave a darkened solution, HCl evolved, and the temperature rose to 27°; after 24 hrs. at room temperature the solution when filtered into 75 ml. cold H<sub>2</sub>O reached 87°; cooling by 25 ml. more cold H<sub>2</sub>O, removing 1.1 g. IX, evaporating the filtrate to dryness, and extracting with Et<sub>2</sub>O gave 7.37 g. I. 2H<sub>2</sub>O, m. 88-92°; purification raised the m. p. to 103-4°. The Et<sub>2</sub>O insoluble residue on extraction with MeOH gave 2.5 g. of a brown solid which may be (C<sub>12</sub>H<sub>9</sub>FeSO<sub>3</sub><sup>-</sup>)<sub>2</sub>Fe.4H<sub>2</sub>O. Addition of concentrated NH<sub>4</sub>OH to the MeOH solution gave a brown precipitate and evaporation of the filtrate yielded the NH<sub>4</sub> salt of I as the monohydrate. I with CH<sub>2</sub>N<sub>2</sub> in Et<sub>2</sub>O gave 95 percent Me ferrocenesulfonate, m. 54-5° (light). X (5.8 g.) added dropwise in three min. to 4.6 g. IX in 75 ml. Ac<sub>2</sub>O caused the temperature to rise from 25° to 40°; the mixture was stirred 16 hrs., set aside 6 hrs., and the precipitated ferrocenedisulfonic acid (XI) converted into five g. of the diNH<sub>4</sub> salt by solution in concentrated NH<sub>4</sub>OH, evaporation to dryness and crystallization. The Ac<sub>2</sub>O mother liquors gave 0.8 g. I and 1.75 g. of its ferrous salt. Free XI is very hygroscopic and rapidly becomes blue on exposure to air, but may be stored under anhydrous Et<sub>2</sub>O for several months; di-Me ester, plates, m. 142-3° (Et<sub>2</sub>O). Crude I (62 g.) added portionwise at 50° to 240 ml. PCl<sub>3</sub> at such a rate as to maintain gentle refluxing, the mixture heated until the evolution of HCl ceased, diluted with ligroine, filtered, and the filtrate evaporated gave 48.1 g.

II, m. 100° (ligroine), darkening rapidly in moist air. II (7.11 g.) in 100 ml. Et<sub>2</sub>O was added during 35 min. to 3.8 g. LiAlH<sub>4</sub> in 150 ml. Et<sub>2</sub>O under N, the mixture refluxed 18 hrs., and 5 ml. EtOAc added, then wet Et<sub>2</sub>O, and 300 ml. 3.5N H<sub>2</sub>SO<sub>4</sub>, giving III as a foul-smelling oil, b<sub>0.005</sub> 110°, which formed orange crystals at -70°. A stream of air passed 18 hrs. through a solution of crude III in 100 ml. alcohol, 250 ml. H<sub>2</sub>O, and 100 ml. NH<sub>4</sub>OH precipitated 5.21 g. VIII as a yellow powder, m. 192° (C<sub>6</sub>H<sub>6</sub>). In only one of several such expts. chromatography yielded a small by-product of unknown structure, plates, m. 54°. VIII was reduced back to III by LiAlH<sub>4</sub> by the method described above except that the reflux period was 1.5 hrs. and tetrahydrofuran was used to dissolve the VIII. When catalytic hydrogenation of II was attempted with 10 percent Pd-C and Et<sub>2</sub>O, both the rate of H uptake and the yields of products were very variable. The only products isolated after extraction with H<sub>2</sub>O and chromatography were I from the aqueous extract and VIII from the chromatogram. Crude III, prepared from 1.08 g. VIII, and seven ml. AcCl refluxed 1 hr. and kept overnight gave 0.7 g. VII, m. 56-7° (ligroine). VIII (0.35 g.) was obtained from the CHCl<sub>3</sub> extract of the aqueous suspension remaining after the above Et<sub>2</sub>O extraction. Crude III prepared from 7.11 g. II treated with 4 g. NaOH in 50 ml. deaerated H<sub>2</sub>O, cooled, and the mixture shaken 15 min. with 3.15 g. Me<sub>2</sub>SO<sub>4</sub>, warmed 15 min. to 60°, cooled, extracted with CHCl<sub>3</sub>, washed, dried, evaporated to 5.9 g. oil, and chromatographed in ligroine on Al<sub>2</sub>O<sub>3</sub> gave 5.17 g. IV, b<sub>0.1</sub> 97.5-8.0°, n<sub>D</sub><sup>25</sup> 1.6488. No methylation occurred when a solution of the III in Et<sub>2</sub>O was treated with excess CH<sub>2</sub>N<sub>2</sub>; only VIII was recovered on chromatography of the product. III prepared from 1.085 g. VIII, converted into its Na salt, refluxed 5.5 hrs. with 1.2 g. CH<sub>2</sub>:CHCH<sub>2</sub>Br in 50 ml. Me<sub>2</sub>CO, the solvent removed, the residue dissolved in CHCl<sub>3</sub>, dried, evaporated, and the residue chromatographed in ligroine on Al<sub>2</sub>O<sub>3</sub> gave 0.4 g. V, m. 32°. C<sub>6</sub>H<sub>6</sub> elution gave 0.56 g. unchanged VIII. Crude III (from 2.6 g. II) mixed with 0.28 g. KOH, 2.8 g. anhydrous K<sub>2</sub>CO<sub>3</sub>, 0.86 g. ClCH<sub>2</sub>-CO<sub>2</sub>H, and 50 ml. Me<sub>2</sub>CO, the mixture refluxed three hrs., left overnight, evaporated, the residue dissolved in five g. KOH in 40 ml. H<sub>2</sub>O, the solution aerated 18 hrs., the 0.93 g. precipitated VIII removed, and the filtrate acidified, and extracted with Et<sub>2</sub>O gave 1.06 g. VI, slightly hygroscopic. m. 110.5°. II (1.42 g.) and 20 ml. NH<sub>4</sub>OH in 20 ml. Me<sub>2</sub>CO heated one hr. on the steam bath gave 1 g. ferrocenesulfonamide, m. 175° (alcohol). II (1.74 g.) and 0.57 g. IX in 75 ml.

$\text{CHCl}_3$  under N at  $0^\circ$  treated with 1.63 g.  $\text{AlCl}_3$  the mixture stirred 16 hrs., 100 g. ice, three ml. concentrated  $\text{HCl}$ , and a little  $\text{TiCl}_3$  added, and the organic layer separated, washed, dried, evaporated, and chromatographed on  $\text{Al}_2\text{O}_3$  in ligroine gave 76 percent unchanged IX and 115 mg. VIII. A minute amount of a third, unidentified substance, m.  $65^\circ$  was eluted. The infrared spectra of some of the products are collected in a table and compared with those of corresponding  $\text{C}_6\text{H}_6$  derivatives.

297. Nesmeyanov, A. N., Perevalova, E. G., Leont'eva, L. I., and Ustynyuk, Y. A.,

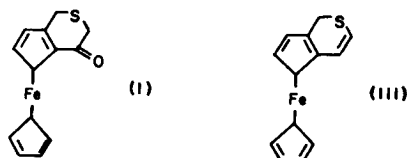
FERROCENYLMETHYL MERCAPTAN AND METHYL FERROCENYLMETHYL SULFIDE, Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 9, 1965, pp. 1696-1697 (In Russian).

A solution of 9.5 g.  $\text{NaOH}$  in 100 cc.  $\text{H}_2\text{O}$  was cooled in ice and saturated with  $\text{H}_2\text{S}$  and added to a solution of 29.6 g. (benzyl) (dimethyl) (ferrocenylmethyl) ammonium chloride (I). The mixture was heated 70 min. on a  $\text{H}_2\text{O}$  bath, cooled, and extracted with  $\text{Et}_2\text{O}$ , and the  $\text{Et}_2\text{O}$  solution washed with  $\text{H}_3\text{PO}_4$  and dried over  $\text{MgSO}_4$ . The  $\text{Et}_2\text{O}$  evaporated in vacuo gave 90 percent ferrocenylmethyl mercaptan (II), m.  $65^\circ$  (petroleum ether-benzene),  $\nu$  1002 and 1106  $\text{cm}^{-1}$ . An aqueous  $\text{NaOH}$  solution of II was treated with  $\text{BzCl}$  and extracted with  $\text{Et}_2\text{O}$ , the  $\text{Et}_2\text{O}$  solution washed with  $\text{H}_3\text{PO}_4$  and dried over  $\text{MgSO}_4$ , and the  $\text{Et}_2\text{O}$  evaporated gave benzoyl ferrocenylmethyl mercaptan (III), m.  $103.5-4^\circ$  (absolute  $\text{EtOH}$ ). A solution of 2.3 g. II in 20 cc. 10 percent aqueous  $\text{KOH}$  was added to a solution of 3.9 g.  $\text{ClCH}_2\text{CO}_2\text{H}$  in six cc. 10 percent  $\text{KOH}$ , the solution heated 50 min. on a steam bath, cooled, and acidified with  $\text{H}_3\text{PO}_4$ , the acid solution extracted with  $\text{Et}_2\text{O}$ , washed with  $\text{NaHCO}_3$ , dried, and evaporated to give 90 percent S-ferrocenylmethylthioacetic acid (IV), m.  $120-1^\circ$  [benzene-petroleum ether (2:1)]. To a solution of five g. II in 7.5 cc. 40 percent aqueous  $\text{NaOH}$  and 35 cc.  $\text{H}_2\text{O}$  was added 2.4 cc.  $\text{Me}_2\text{SO}_4$ . The mixture was heated one hr. on a steam bath, cooled, and extracted with  $\text{Et}_2\text{O}$ , the  $\text{Et}_2\text{O}$  solution washed with  $\text{H}_2\text{O}$  and dried over  $\text{CaCl}_2$ , the  $\text{Et}_2\text{O}$  evaporated, and the residue chromatographed on  $\text{Al}_2\text{O}_3$  to give 42 percent methyl ferrocenylmethyl sulfide (V), m.  $44-5^\circ$  (heptane). Treatment of 1.61 g. V with Li in tetrahydrofuran 30 min. at  $-5^\circ$  and 26 hrs. at ambient temperature, followed by a  $\text{H}_2\text{O}$

work-up gave a residue, which was taken up in petroleum ether and chromatographed on  $\text{Al}_2\text{O}_3$  to yield 55 percent methylferrocene, 8 percent V, and 7 percent 1,2-diferrocenyethane.

298. Nesmeyanov, A. N., Perevalova, E. G., Leont'eva, L. I., and Ustynyuk, Y. A.,  
SYNTHESIS OF 1,2-DISUBSTITUTED FERROCENES,  
Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 10, 1965, pp. 1882-1884 (In Russian).

Stirring 5.91 g. S-ferrocenylmethylthioglycolic acid with 10 g.  $(\text{COCl})_2$  in  $\text{C}_6\text{H}_6$ - $\text{CH}_2\text{Cl}_2$  under N atm. four hrs. gave after concentration in vacuo, a solution of the acyl chloride which diluted with  $\text{CH}_2\text{Cl}_2$  and treated with 4.72 ml.  $\text{SnCl}_4$  in  $\text{CH}_2\text{Cl}_2$  at  $-70^\circ$ , kept 40 min. at this temperature, and poured on ice HCl, gave 1,2-(2-thia-4-oxotetramethylene)ferrocene (I), m.  $66-7^\circ$ , which decomposed during attempted chromatographing on  $\text{Al}_2\text{O}_3$  or  $\text{SiO}_2$ . I and Raney Ni in absolute EtOH in 6.5 hrs. refluxing followed by chromatographic separation of the products on thin-layer of  $\text{Al}_2\text{O}_3$  in  $\text{C}_6\text{H}_6$ -petr. ether, gave 51 percent 1-methyl-2-ethylferrocene, b<sub>2</sub>  $90.5-2.5^\circ$ ,  $n_D^{20}$  1.6026, and 25 percent 1-methyl-2-acetylferrocene, m.  $61-1.5^\circ$ . In 5.5 hrs. the yields were 28 percent



and 60 percent, respectively. I and  $\text{LiAlH}_4$  in  $\text{Et}_2\text{O}$  under N gave 3.5 hrs. at room temperature 42 percent 1,2-(2-thia-4-hydroxytetramethylene)ferrocene (II), m.  $78^\circ$ . I added to the mixture of 5.3 g.  $\text{AlCl}_3$  and one g.  $\text{LiAlH}_4$  in  $\text{Et}_2\text{O}$  and stirred five hrs. at reflux, gave 30 percent methylferrocene, 5 percent II, and 40 percent 1,2-(2-thiatetramethylene)ferrocene, m.  $73.5-4.5^\circ$ , separated chromatographically. Shorter reaction intervals resulted in reduced yields of this product and increased yields of II. In one experiment a product, m.  $83-4^\circ$ , was obtained which appeared to be III.

99. Schlogel, K. and Pelousek, H.,

FERROCENE DERIVATIVES. IX. PREPARATION AND ACETYLATION OF THIENYL DERIVATIVES OF FERROCENE. STUDY OF THE REACTIVITY OF AROMATIC SYSTEMS, Ann., Vol. 651, 1962, pp. 1-10, (cf. CA 56, 12938f).

(Reaction mixtures and products were analyzed by thin layer chromatography). To 21 g. ferrocene (I) and 14 g.  $\text{AlCl}_3$  in 100 cc. absolute  $\text{CH}_2\text{Cl}_2$  was added dropwise during 30 min. 15.4 g. 2-thenoyl chloride (II) in 50 cc. absolute  $\text{CH}_2\text{Cl}_2$  with stirring, the mixture refluxed and stirred 5 hrs., cooled, treated with ice, the organic layer separated, washed repeatedly with  $\text{H}_2\text{O}$  and aqueous  $\text{NaHCO}_3$ , dried, evaporated, and the residue chromatographed in  $\text{C}_6\text{H}_6$  on  $\text{Al}_2\text{O}_3$  to give three g. recovered I and 19.6 g. 2-thenylferrocene (III), m.  $124-6^\circ$  ( $\text{C}_6\text{H}_6$ -petr. ether). To 4.8 g. II and 4.4 g.  $\text{AlCl}_3$  in 30 cc. absolute  $\text{CH}_2\text{Cl}_2$  was added dropwise 2.6 g. I in 30 cc.  $\text{CH}_2\text{Cl}_2$  with stirring, the mixture refluxed eight hrs., worked up as above, and the product chromatographed on  $\text{Al}_2\text{O}_3$  in  $\text{C}_6\text{H}_6$  with increasing amounts of  $\text{CHCl}_3$  to give 15 percent III and 37 percent 1,1'-di(2-thenoyl)ferrocene (IV), m.  $166-8^\circ$  ( $\text{C}_6\text{H}_6$ ). With larger amounts it was more expedient to effect the separation of III and IV by recrystallization from  $\text{C}_6\text{H}_6$ , in which III was much more soluble.  $\text{AlCl}_3$  (2.5 g.) in 50 cc. absolute  $\text{Et}_2\text{O}$  added to one g.  $\text{LiAlH}_4$  in 50 cc. absolute  $\text{Et}_2\text{O}$  with stirring and ice cooling, after 10 min. the mixture treated dropwise with five g. III in 100 cc. absolute tetrahydrofuran with stirring, stirred 30 min. at room temperature, treated with 200 cc. ice  $\text{H}_2\text{O}$ , and the product isolated with  $\text{Et}_2\text{O}$  gave 4.3 g. 2-thenylferrocene (V), m.  $60-2^\circ$  (petr. ether). III (15.7 g.) in 100 cc. absolute  $\text{EtOH}$  added in small portions to 10 g. finely divided Na in 100 cc. absolute xylene at  $90^\circ$  with stirring, refluxed and stirred 2 hrs., the solution evaporated in vacuo, the residue treated portionwise with 350 cc.  $\text{H}_2\text{O}$ , the product (15 g.) isolated with  $\text{Et}_2\text{O}$ , distilled in vacuo, the distillate [six g. oil  $b_{0.3}$   $120-40^\circ$  (air bath temperature) (partial decomposition)] chromatographed on  $\text{Al}_2\text{O}_3$ , and developed with  $\text{C}_6\text{H}_6$ - $\text{CHCl}_3$  gave 2.5 g. V, m.  $60-2^\circ$  (petr. ether), and 2.5 g. cyclopentadienyl [(1-hydroxypentyl) cyclopentadienyl] iron,  $b_{0.2}$   $115-25^\circ$  (air bath temperature),  $n_D^{20}$  1.5940. Reduction of  $\alpha$ -hydroxy-2-thenylferrocene (IV) with  $\text{LiAlH}_4$ - $\text{AlCl}_3$  as above gave almost quantitative V. Reduction of IV with  $\text{LiAlH}_4$ - $\text{AlCl}_3$  gave 95 percent 1,1'-di(2-thenyl)ferrocene (VII), m.  $61-3^\circ$  ( $\text{C}_6\text{H}_6$ -petr. ether).



Similar reduction of 1, 1'-bis ( $\alpha$ -hydroxy-2-thenyl) ferrocene (VIII) also gave VII. IV reduced with Na and EtOH as above and the crude product chromatographed in  $C_6H_6$  on  $Al_2O_3$  gave 38 percent VII and 48 percent 1-pentyl-1'-(2-thenyl) ferrocene,  $b_{0.4}$  180-90° (air bath temperature). III (0.6 g) in 20 cc. absolute tetrahydrofuran treated with 0.11 g.  $LiAlH_4$ , heated 15 min. on a  $H_2O$  bath, treated with a min. of  $H_2O$ , the precipitate filtered off, washed with  $Et_2O$ , and the combined organic solutions evaporated in vacuo gave 0.57 g. VI, m. 70-2° (petr. ether). Similar reduction of IV gave 90 percent VIII, m. 100-5° ( $C_6H_6$ -petr. ether). V (0.8 g.) in 160 cc. EtOH refluxed 90 min. with 14 g. Raney Ni, filtered, and the filtrate fractionated gave 0.58 g. pentylferrocene (IX),  $b_{0.05}$  80-90° (air bath temperature),  $n_D^{20}$  1.5711. Valerylferrocene (X) (2.0 g.) boiled 30 hrs. with 7.5 g. Zn-Hg in eight cc. concentrated HCl and 13 cc. PhMe (5 3-cc. portions concentrated HCl added at intervals) gave 90 percent IX. X treated with  $LiAlH_4-AlCl_3$  gave almost quantitative IX. Desulfurization of VII with Raney Ni gave 70 percent 1, 1'-dipentylferrocene (XI),  $b_{0.04}$  125-35° (air bath temperature),  $n_D^{20}$  1.5428. Clemmensen reduction of  $LiAlH_4-AlCl_3$  reduction of 1, 1'-divalerylferrocene (XII) gave 70 to 95 percent XI. I (5.6 g.), 3.7 g.  $BuCOCl$  (XIII), and 4.2 g.  $AlCl_3$  in absolute  $CH_2Cl_2$  refluxed two hrs., worked up as in the preparation of III, and the product chromatographed in  $C_6H_6$  on  $Al_2O_3$  gave 4.5 g. X,  $b_{0.01}$  110-20° (air bath temperature), m. 36-8°. I (3.35 g.) in absolute  $CH_2Cl_2$  added dropwise to 4.5 g. XIII and five g.  $AlCl_3$  in  $CH_2Cl_2$  (total amount.  $CH_2Cl_2$  was 100 cc.), refluxed five hrs., worked up as above, and purified by chromatography gave 80 percent XII, m. 33-6° (petr. ether). Desulfurization of IV with Raney Ni gave 45 percent XII.  $AcCl$  (0.43 g.) in 10 cc.  $CH_2Cl_2$  added dropwise to 1.4 g. V and 0.73 g.  $AlCl_3$  in 50 cc. absolute  $CH_2Cl_2$  with stirring, the mixture refluxed and stirred six hrs., decomposed with ice  $H_2O$ , the organic layer separated, washed with aqueous  $NaHCO_3$  and  $H_2O$ , dried, evaporated, and the residue (one g.) chromatographed on  $Al_2O_3$  in  $C_6H_6$  with increasing amounts of  $CHCl_3$  gave (1) 0.1 g. recovered V, (2) 0.15 g. impure compound, which was repeatedly recrystallized from  $Et_2O$ -petr. ether to yield 0.03 g. (5-acetyl-2-thenyl) ferrocene (XIV), m. 145-7°, and (3) 0.65 g. impure compound, which was chromatographed on  $Al_2O_3$  and recrystallized from  $C_6H_6$ -petr. ether to yield 0.06 g. 1-(5-acetyl-2-thenyl) 1'-acetylferrocene (XV), m. 110-16°. V (0.9 g.) in 40 cc.  $CH_2Cl_2$  added dropwise to 1.01 g.  $AcCl$  and 1.8 g.  $AlCl_3$  in 50 cc. absolute

$\text{CH}_2\text{Cl}_2$  with stirring, refluxed and stirred four hrs., worked up, and the product chromatographed in  $\text{C}_6\text{H}_6$  on  $\text{Al}_2\text{O}_3$  gave 1.2 g. 1-(5-acetyl-2-thenyl)-1'3-diacetylferrocene, m. 123-5° (MeOH-petr. ether). XIV (0.06 g.) refluxed one hr. with one g. Raney Ni in 100 cc. EtOH gave 0.03 g. (6-hydroxy-1-heptyl)ferrocene,  $b_{0.3}$  145-50° (air bath temperature). Et 2-thiophenecarboxylate (XVI) (six g.) in 10.4 g.  $\text{Ac}_2\text{O}$  containing 0.7 g. anhydrous  $\text{ZnCl}_2$  heated three hrs. on a  $\text{H}_2\text{O}$  bath, concentrated in vacuo, the residue treated with  $\text{H}_2\text{O}$ , and the product isolated with  $\text{Et}_2\text{O}$  gave 0.6 g. 5-Ac derivative of XVI,  $b_{0.3}$  110° (bath temperature), m. 49-51°, saponified (three hrs. with alcohol-KOH) to 0.35 g. 5-acetyl-2-thiophenecarboxylic acid (XVII), m. 203-6° (EtOH- $\text{H}_2\text{O}$ ). XVII (2 g.) and five cc.  $\text{SOCl}_2$  heated 45 min. on a  $\text{H}_2\text{O}$  bath and evaporated gave 2 g. acid chloride (XVIII) of XVII, m. 77-9°. I (2.23 g.), 2.9 g.  $\text{AlCl}_3$ , and 1.9 g. XVIII in  $\text{CH}_2\text{Cl}_2$  treated as in the preparation of III, the resulting crude (5-acetyl-2-thenoyl)ferrocene reduced with  $\text{LiAlH}_4$ - $\text{AlCl}_3$ , and the product chromatographed on  $\text{Al}_2\text{O}_3$  gave 1.3 g. (5-ethyl-2-thenyl)ferrocene,  $b_{0.001}$  115-20°, identical (infrared absorption spectrum and thin layer chromatogram) with the product obtained by reduction of XIV with  $\text{LiAlH}_4$ - $\text{AlCl}_3$ . Friedel-Crafts acetylation of VII with two moles  $\text{AcCl}$ - $\text{AlCl}_3$  gave a mixture of four compounds; the main fraction (60 percent of the mixture) was shown (by its anal. data) to be 1,1'-bis(5-acetyl-2-thenyl)ferrocene; none of the fractions could be obtained crystalline. Benzylferrocene (XIX) [Rausch, et al., CA 52, 3794e] refluxed three hrs. with 0.8 g.  $\text{AcCl}$  and 1.33 g.  $\text{AlCl}_3$  in  $\text{CH}_2\text{Cl}_2$  and the crude product (2 g.) chromatographed in  $\text{C}_6\text{H}_6$  on  $\text{Al}_2\text{O}_3$  gave 0.35 g. 1-benzyl-1'-acetylferrocene, m. 78 to 81° (petr. ether). Friedel-Crafts acetylation of XIX with four moles  $\text{AcCl}$ - $\text{AlCl}_3$  like in the preparation of XV gave a small amount of fraction (not further investigated), 40 percent 1-(4-acetylbenzyl)-1',3'-diacetylferrocene, m. 132-4° ( $\text{C}_6\text{H}_6$ - $\text{Et}_2\text{O}$ ), and 27 percent tetra-Ac compound, m. 114-17° ( $\text{C}_6\text{H}_6$ - $\text{Et}_2\text{O}$ ), in which each ring contained an Ac group but the position of fourth Ac group was unknown, although its position appeared more likely to be in the benzene nucleus (ortho to the  $\text{CH}_2$  group) than in either of the cyclopentadiene rings.

300. Ushenko, I. K., Zhikhareva, K. D., and Rodova, F. Z., POLYMETHINE DYES CONTAINING THE FERROCENE RESIDUE. I. SYNTHESIS OF FERROCENYLBENZOTHIAZOLES AND PREPARATION OF THIACYANINES FROM THEM, Zhurnal Obshchei Khimii, Vol. 33, No. 3, 1963, pp. 798-804.

Ferrocene heated with (2-methyl-6-benzothiazolyl) dimethyltriazene in AcOH at 45 to 60° for 40 min. gave after an aqueous treatment and separation from ferrocene by adsorption on Al<sub>2</sub>O<sub>3</sub> and successively elution with C<sub>6</sub>H<sub>6</sub>, then with hot MeOH, 15.7 percent 2-methyl-6-ferrocenylbenzothiazole (I) red-brown, m. 154-5°; I was formed in 15 percent yield by treatment of diazotized 2-methyl-6-aminobenzothiazole with ferrocene at -10° in Et<sub>2</sub>O mixed with aqueous NaOAc solution, warming gradually to room temperature, and heating one hr. to 30°; this reaction also gave 0.35 percent yellow-orange bis (2-methyl-6-benzothiazolyl) ferrocene, m. 240°, which was retained more tenaciously by Al<sub>2</sub>O<sub>3</sub>. I also formed in 29 percent yield by the latter reaction if the aqueous NaOAc solution was added at about -10°. The first method applied to (2-methyl-5-benzothiazolyl) dimethyltriazene gave 14 percent orange 2-methyl-5-ferrocenylbenzothiazole (II), m. 183-4°; II was formed in 15 percent yield by the second method, along with 1.6 percent bis (2-methyl-5-benzothiazolyl) ferrocene, m. 260-1°; the third method gave a 27 percent yield of II. I and p-MeC<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>Et heated at 145-50° for three hrs. gave the quaternary salt which was refluxed with Hc(OEt)<sub>3</sub> in pyridine for 20 min. and treated with KI to give 55 percent green 3,3'-diethyl-6,6'-diferrocenylthiacarbocyanine iodide, decomposed 252°, λ<sub>max</sub> 608 mμ; the corresponding bromide was bronze colored, decomposed 245°. Similarly, II gave the quaternary salt with p-MeC<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>Et which gave as above 66 percent bronze colored 3,3'-diethyl-5,5'-diferrocenylthiacarbocyanine iodide, decomposed 265°, λ<sub>max</sub> 592 mμ; the corresponding bromide, deep green, decomposed 257°. I, p-MeC<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>Et, and 3-ethyl-5-(acetanilidomethylene) rhodanine in EtOH-Et<sub>3</sub>N gave after brief refluxing 62 percent red 3-ethyl-5-[(3-ethyl-6-ferrocenyl-2-benzothiazolinyldene) ethylidene] thiazolidine-2-thione-4-one, m. 294°, λ<sub>max</sub> 543 mμ; similarly was prepared 37 percent violet 3-ethyl-5-[(3-ethyl-5-ferrocenyl-2-benzothiazolinyldene) ethylidene] thiazolidine-2-thione-4-one, m. 272°, λ<sub>max</sub> 535 mμ. Formylferrocene and 2-methylbenzothiazole-EtI refluxed in AcOH-Et<sub>3</sub>N-pyridine for 10 min., then treated with KI in aqueous

AcOH, gave 22 percent violet 2-( $\beta$ -ferrocenylvinyl) benzo-thiazole-EtI, decomposed 194-5°; the perchlorate exploded violently at 153°. The ethiodide had adsorption maximum at 405 and 601 m $\mu$ .

#### L. Silicon Containing Derivatives

301. Babare, L. V., Nametkin, N. S., and Chernysheva, T. I., METHOD OF OBTAINING ORGANOSILICON COMPOUNDS CONTAINING A FERROCENYL RADICAL (Foreign Title Not Available), Translated into English from Russian from Soviet Patent No. 165718 by the Air Force Systems Command, Foreign Technology Division, Wright-Patterson Air Force Base, Ohio, 24 June 1965, Report No. FTD-TT-65-465/1 + 4, AD-619 426, N66-10379 (Application No. 851651/23-4, 8 August 1963).

The invention involves a method of obtaining organosilicon compounds which contain a ferrocenyl radical which has the distinguishing feature that, for the purpose of obtaining compounds with heightened heat resistance, silylferrocenes which contain the bond Si-H are subjected to interaction with di-(vinylarylalkyl)-disiloxane or di-(vinylalkylaryl)-silylbenzene with heating up to 180-200°C in the presence of platinohydrochloric acid as a catalyst.

302. Berdichevskaya, K. M., Chugunov, V. S., and Petrov, A. D., SYNTHESIS OF SOME FLUORINE-CONTAINING SILYL-FERROCENES, Doklady Akademiyi Nauk SSSR, Vol. 151, No. 6, 1963, pp. 1319-1321.

To 24 g. Mg under Et<sub>2</sub>O was added 225 g. m-BrC<sub>6</sub>H<sub>4</sub>CF<sub>3</sub> and 142 g. Me<sub>2</sub>SiCl<sub>2</sub> in Et<sub>2</sub>O and the mixture refluxed six hrs. to give 43 g. crude product, b<sub>15</sub> 90-100°, containing m-F<sub>3</sub>CC<sub>6</sub>H<sub>4</sub>SiMe<sub>2</sub>Cl. Similarly, Mg, SiCl<sub>4</sub>, and CF<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>Cl in Et<sub>2</sub>O gave crude (CF<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>SiCl (I), b<sub>20</sub> 80-120°. I (58 g.) was added to a mixture of 18 g. ferrocene and BuLi in Et<sub>2</sub>O, prepared in three days at room temperature, and the mixture stirred three days to yield some (CF<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>O, m. 141-2°, and 7.5 g. tris ( $\gamma$ ,  $\gamma$ ,  $\gamma$ -trifluoropropyl) silylferrocene, b<sub>12</sub> 180-205°, m. 105°. The residues gave some yellow bis[ tris ( $\gamma$ ,  $\gamma$ ,  $\gamma$ -trifluoropropyl) silyl] ferrocene, m. 155°. Similarly was prepared a low yield of dimethyl(m-trifluoromethylphenyl) silylferrocene, b<sub>17</sub> 205-32°, m. 50°, and bis[ dimethyl(trifluoromethylphenyl) silyl] ferrocene, b<sub>7</sub> 232-5°, m. 71°.

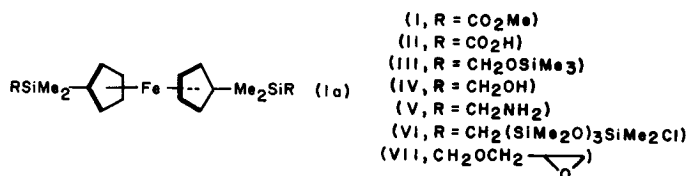
Ferrocene treated two days with BuLi in tetrahydrofuran, followed by  $\text{Pr}_3\text{SiBr}$  40 hrs. at room temperature and three hrs. at reflux, gave bis(tripropylsilyl)ferrocene,  $b_1$  227-33°,  $n_D^{20}$  1.5203,  $d_{20}$  1.0214.

303. Dickey, C. R., Mailey, E. A., and Matthews, V. E.,  
1,1'-BIS(TRIALKYL-SILYL-CYCLOPENTADIENYL) IRONS,  
U. S. Patent 3,062,854 (Cl. 260-439), 6 November 1962,  
Applied 5 July 1960, 3 pp.

Compositions where high temperature operating conditions are involved, were prepared by treating, in an  $\text{Et}_2\text{O}$  solvent at -25 to 35°, a trialkylsilicon halide with a cyclopentadienyl-sodium to give a trialkylsilylcyclopentadiene, contacting the above reaction mixture at between -25 and 25° with a  $\text{H}_2\text{O}$ -immiscible ether and an aqueous acid and separating a solution of substantially pure trialkylsilylcyclopentadiene. This, without isolation, was treated with Na in an ether at -25 to 35° to give a trialkylsilylcyclopentadienylsodium, which was treated in an ether solvent at 0-100° with an Fe halide to give a 1,1'-bis(trialkylsilylcyclopentadienyl)iron; the latter was recovered by removing the solvent by film distillation of the residue with a conventional molecule still. For example, 1,1'-bis(tridodecylsilylcyclopentadienyl)iron,  $b_{3-5\mu}$  290-5°,  $n_D^{20}$  1.4922, was prepared by treatment as above in tetrahydrofuran of tridodecylchlorosilane with cyclopentadienylsodium.

304. Greber, G. and Hallensleben, M. L.,  
SYNTHESIS AND POLYMERIZATION OF BIFUNCTIONAL  
ORGANOSILICON FERROCENE DERIVATIVES, Makromolekulane Chemie, Vol. 92, 1966, pp. 137-148 (In German) (cf. CA 63, 16479e).

The addition of 1,1'-bis(dimethylhydrosilyl)ferrocene to functionally substituted olefins with  $\text{H}_2\text{PtCl}_6$  as catalyst produces bifunctional compounds Ia ( $b.p./\text{mm.}$ ,  $d^{20}$ , and  $n_D^{20}$  given): I, 170-5°/0.003, 1.1923, 1.5373; II, 187-94°/0.001,



1.1547, 1.5208; III, -, 1.0467, 1.5139; IV, -, 1.0941, 1.5658; V, 143-8/0.001, 1.1083, 1.5615; VI, -, 1.0485, 1.4779; VII, -, 1.1467, 1.5413. These ferrocene derivatives react with suitable partners to form polymers; IV forms polyesters with terephthaloyl chloride and polyurethans with p-phenylene diisocyanate, II forms polyamides with hexamethylene diamine, VII reacts with diamines to form glassy insoluble polymers (also with acid catalysts such as  $\text{AlCl}_3$ ); the thermal stability of some of these polymers was investigated between 200-300°.

305. Knox, G. R., Munro, J. D., Pauson, P. L., Smith, G. H., and Watts, W. E.,  
SOME SUBSTITUTED CYCLOPENTADIENYL DERIVATIVES  
OF NICKEL, COBALT, IRON, MOLYBDENUM, AND  
TITANIUM, Journal of Chemical Society, 1961, pp. 4619-4624.

Tetrapyridinenickel chloride (I) (20 g.) in 40 ml. tetrahydrofuran (THF) was added to  $\text{C}_5\text{H}_5\text{Na}$  (prepared from 2.07 g. Na and 6.6 g.  $\text{C}_6\text{H}_6$  in 100 ml. THF under N), the mixture stirred 30 min., evaporated in vacuo, and the product isolated by sublimation or by extraction with ligroine or  $\text{Et}_2\text{O}$  to give 4.83 g.  $(\text{C}_5\text{H}_5)_2\text{Ni}$ , m. 172-3° (decomposition); yields up to 70 percent were obtained in larger runs with Soxhlet extraction. Dimethylfulvene (II) (2.12 g.) in 25 ml.  $\text{Et}_2\text{O}$  was added dropwise to 0.19 g.  $\text{LiAlH}_4$  in 10 ml.  $\text{Et}_2\text{O}$  under N, a slurry of 4.46 g. I in 40 ml. THF added, the mixture stirred 1 hr., evaporated in vacuo, and the residue chromatographed on  $\text{Al}_2\text{O}_3$  to give 0.99 g. air-sensitive  $(\text{Me}_2\text{CHC}_5\text{H}_4)_2\text{Ni}$ , purified by distillation  $b_{0.3}$  128° (bath temperature). Similarly, with  $\text{PhLi}$  (prepared from 3.5 g.  $\text{PhBr}$  and 0.33 g. Li) instead of  $\text{LiAlH}_4$  and isolation by evaporation of the filtered reaction mixture in vacuo, 2.68 g.  $(\text{PhMe}_2\text{CC}_5\text{H}_4)_2\text{Ni}$  (III), m. 109-10° (ligroine) was obtained. A solution of 2.12 g. III in 75 ml. ligroine was saturated with NO, filtered evaporated in vacuo, the residue chromatographed on  $\text{Al}_2\text{O}_3$ , and the main band distilled to give 0.69 g.  $\text{PhMe}_2\text{CC}_5\text{H}_4\text{NiNO}$ ,  $b_{0.3}$ , 146°.  $\alpha$ -Ferrocenylfulvene (IV) (CA 56, 12939c) (1.14 g.) in 25 ml.  $\text{Et}_2\text{O}$  was added dropwise to  $\text{PhLi}$  (prepared in  $\text{Et}_2\text{O}$  from 1.60 g.  $\text{PhBr}$  and 0.2 g. Li) under N, the mixture stirred 1.5 hrs.,  $\text{FeCl}_2$  (prepared from 0.003 mole  $\text{FeCl}_3$ ) in 20 ml. THF added, the mixture stirred 66 hrs., poured into ice- $\text{H}_2\text{O}$ , extracted with  $\text{Et}_2\text{O}$ , the extract washed with  $\text{H}_2\text{O}$  and evaporated in vacuo, and the residue chromatographed on  $\text{Al}_2\text{O}_3$  to give 5.5 percent IV and 21 percent 1,1'-bis( $\alpha$ -ferrocenylbenzyl)ferrocene, m.

194-6° (ligroine). Similarly, from 0.005 mole  $\text{CoCl}_2$  was obtained an aqueous solution of 1,1'-bis( $\alpha$ -ferrocenylbenzyl) cobalticenium chloride, from which was precipitated the picrate, reineckate, and perchlorate; these salts decomposed upon recrystallization. Tetramethylformamidinium perchlorate (Arnold, CA 53, 12168b) (10 g.) was added in small portions to  $\text{C}_5\text{H}_5\text{Na}$  (prepared from 1.4 g. Na and excess  $\text{C}_5\text{H}_6$ ) in 180 ml. THF, the mixture stirred 12 hrs., treated with 20 ml. MeOH, added to 250 ml.  $\text{H}_2\text{O}$ , extracted with  $\text{Et}_2\text{O}$ , and the extract dried and evaporated in vacuo to give 78 percent  $\alpha$ -dimethylaminofulvene (V), m. 64-6° (ligroine). V (1.16 g.) in 20 ml.  $\text{Et}_2\text{O}$  was added dropwise to MeLi (from 0.28 g. Li and 2.84 g. MeI) in 40 ml.  $\text{Et}_2\text{O}$  under N, the mixture stirred 4 hrs., treated with  $\text{FeCl}_2$  (from 2.3 g.  $\text{FeCl}_3$ ) in 10 ml. THF, stirred overnight, 10 ml. MeOH added, the mixture poured into  $\text{H}_2\text{O}$ , extracted with  $\text{Et}_2\text{O}$ , and the extract dried and evaporated in vacuo to give 71 percent 1,1'-bis(1-dimethylaminoethyl)ferrocene (VI), b<sub>1</sub> 120° (bath temperature). The dimethiodide of VI was readily hydrolyzed to 2,4-(1,1'-ferrocenylene)-3-oxapentane (two stereoisomers). V (1.21 g) in 10 ml.  $\text{Et}_2\text{O}$  was added dropwise to 0.4 g.  $\text{LiAlH}_4$  in 20 ml.  $\text{Et}_2\text{O}$  under N, the mixture stirred 2 hrs.,  $\text{FeCl}_2$  (from 0.008 mole  $\text{FeCl}_3$ ) in 20 ml. THF added, the mixture stirred overnight, ice added, and the  $\text{Et}_2\text{O}$  layer dried and evaporated in vacuo to give 58 percent 1,1'-bis(dimethylaminomethyl)ferrocene; dimethiodide picrate m. 228° (decomposition) ( $\text{H}_2\text{O}$ -MeOH). Similarly, 0.008 mole  $\text{CoCl}_2$  gave (after thorough extraction of the organic phase with dilute HCl and adjustment of the extract to pH4) an aqueous solution of 1,1'-bis(dimethylaminomethyl) cobalticenium ion, from which was precipitated the reineckate (MeOH) and tetraphenylborate (MeOH) (total, 78 percent). II (21 g.) was added to  $\text{NaNH}_2$  (from 4.6 g. Na) in 200 ml.  $\text{NH}_3$  under N, the mixture stirred 0.5 hr., 200 ml. THF added, and the  $\text{NH}_3$  evaporated; the mixture was treated with 13 g.  $\text{CoCl}_2$ , stirred overnight, poured onto HCl-ice, and extracted with  $\text{Et}_2\text{O}$  to give an aqueous solution of 1,1'-bis(isopropenyl) cobalticenium (III) ion, from which was precipitated the picrate, m. 122.5-3.0° ( $\text{H}_2\text{O}$ ), perchlorate (VII), m. above 145° (aqueous  $\text{NH}_4\text{ClO}_4$ ;  $\text{Me}_2\text{CO}$ - $\text{Et}_2\text{O}$  precipitation), tetraphenylborate ( $\text{Me}_2\text{CO}$ - $\text{H}_2\text{O}$  precipitation), reineckate, tribromide, and tri (or poly) iodide. VII (1 g.) in 25 ml  $\text{CHCl}_3$  at 0° was treated with  $\text{O}_3$  1 hr. at 0.005 g./min., 50 ml.  $\text{H}_2\text{O}$  added, the mixture refluxed 1 hr.,  $\text{CHCl}_3$  then removed by distillation (an aqueous extract of the distillate gave 54 mg.  $\text{CH}_2\text{O}$  as the dimedone derivative), and

half the residue treated with a saturated solution of Reinecke's salt to give 64 percent 1,1'-diacetylcobalticenium reineckate, m. 176-9° (Me<sub>2</sub>CO), and half converted to the tetraphenylborate, m. 195-8°, decomposing from 165° (Me<sub>2</sub>CO). Diazocyclopentadiene (2.76 g.) in 20 ml. Et<sub>2</sub>O was added dropwise to 0.03 mole PhLi in 50 ml. Et<sub>2</sub>O at -30° under N to give a solution of phenylazocyclopentadienyllithium (VIII): 1.94 g. CoCl<sub>2</sub> was added after 30 min., the mixture stirred overnight to room temperature, solvent removed in vacuo, 50 ml. 2N HCl added, the mixture kept 10 min. at 100°, filtered, and cooled to precipitate 71 mg. 1,1'-bis(phenylazo)cobalticenium chloride, m. 138-9°(decomposition) (2N HCl); from half the filtrate was precipitated 1.63 g. reineckate, m. 217-19° (Me<sub>2</sub>CO), and from the remainder 1.45 g. tetraphenylborate, decompose above 160° (Me<sub>2</sub>CO). TiCl<sub>4</sub> (2.84 g.) in 20 ml. THF was added to 0.03 mole VIII, the mixture stirred overnight, solvent removed in vacuo, the residue extracted with C<sub>6</sub>H<sub>6</sub>, and the extract evaporated to give 42.5 percent bis-(phenylazocyclopentadienyl)titanium dichloride, m. 198-204°, decomposing from 175° (benzene-ligroine). II (17 g.) and 17 g. Mo<sub>2</sub>(CO)<sub>6</sub> heated 8.5 hrs. at 120° under N, the mixture evaporated in vacuo, and the residue chromatographed on Al<sub>2</sub>O<sub>3</sub> gave (Me<sub>2</sub>CHC<sub>5</sub>H<sub>4</sub>)Mo<sub>2</sub>(CO)<sub>6</sub> (IX), m. 155-6°, and (CH<sub>2</sub>:CMeC<sub>5</sub>H<sub>4</sub>)(Me<sub>2</sub>CHC<sub>5</sub>H<sub>4</sub>)Mo<sub>2</sub>(CO)<sub>6</sub> (X), m. 119° (ligroine). Elution of six additional bands gave solids with very similar infrared spectra; the first band was probably (CH<sub>2</sub>:CMeC<sub>5</sub>H<sub>4</sub>)<sub>2</sub> - Mo<sub>2</sub>(CO)<sub>6</sub> (XI), and the rest polymers of X and XI. In this reaction, a potential intermediate was (CH<sub>2</sub>:CMeC<sub>5</sub>H<sub>4</sub>)Mo(CO)<sub>3</sub>H (formed by isomerization of a dimethylcarbonium cyclopentadienide), which would be expected (Fischer, et al., CA 50, 6997a) to decompose to dimers, the H adding to olefins present to give mainly X. X absorbed one mole H over 10 percent Pd-C to give quantitative IX.



306. Kumada, M., Mimura, K., Ishikawa, M., and Shiina, K.,  
DISILANYL-SUBSTITUTED FERROCENES, Tetrahedron  
Letters, No. 1, 1965, pp. 83-88.

Pentamethyldisilanylferrocene (I) refluxed two hrs. in extremely dilute EtOH-HCl gave, via vapor phase chromatography, ferrocene (II), ethoxydimethylsilylferrocene,  $\text{Me}_3\text{-SiOEt}$ , and  $(\text{Me}_3\text{Si})_2\text{O}$ ; under similar conditions, 1,1'-bis (pentamethyldisilanyl) ferrocene (III) gave II and 1,3-(1,1'-ferrocenylene) tetramethyldisiloxane, m.  $87-8^\circ$ .  $\text{Me}_3\text{SiSiMe}_2\text{-Cl}$  and  $\text{C}_5\text{H}_5\text{MgBr}$  gave 65 percent  $\text{Me}_3\text{SiSiMe}_2\text{C}_5\text{H}_5$  (IV),  $b_{22} 80^\circ$ ,  $n_D^{20} 1.4913^\circ$ ,  $d_{20} 0.8505$ , and IV with BuLi followed by  $\text{FeCl}_2$  gave 65 percent III. Equimolar amounts IV and cyclopentadiene metalated with BuLi and then treated with  $\text{FeCl}_2$  gave I. The reaction mechanisms were discussed.

307. Mailey, E. A., Dickey, C. R., Goodale, G. M., and Matthews, V. E.,  
SYNTHESIS OF 1,1'-BIS(TRIDODECYLSILYL) FERROCENE,  
Journal of Organic Chemistry, Vol. 27, 1962, pp. 616-619.

The previously unreported 1,1'-bis(tridodecylsilyl) ferrocene (I) was synthesized in a yield of about 54 percent from chlorotridodecylsilane (II) via the intermediate triiododecylsilylcyclopentadiene (III). The procedure utilized modifications of previously developed synthetic methods and should be applicable to the preparation of other disubstituted silylferrocenes. Some aspects of the preparation of the intermediate compounds and the ferrocene derivative were discussed. Dodecylmagnesium bromide (2 moles) in 1150 ml.  $\text{Et}_2\text{O}$  treated dropwise over 1 hr. at ambient temperature, the slurry treated overnight at room temperature, then hydrolyzed, the aqueous layer extracted with  $\text{Et}_2\text{O}$ , the combined  $\text{Et}_2\text{O}$  portions dried and evaporated gave 256 g. tridodecylsilane (IV),  $b_{0.05} 220-35^\circ$ ,  $n_D^{20} 1.4606$ , m.  $16-16.5^\circ$ . IV (306.5 g.) in 310 ml. ethylene dichloride allowed to react at  $0-6^\circ$  with 40 g. Cl, the solvent removed, and the 327 g. yellow oil distilled gave 305 g. II,  $b_{0.03} 228-38^\circ$ ,  $n_D^{20} 1.4647$ , m.  $4-5^\circ$ . Trichlorododecylsilane and dodecylmagnesium bromide (V) gave mixtures of products and attempts to isolate II gave impure material. The following was the best preparation. V (2 moles) in 1050 ml.  $\text{Et}_2\text{O}$  added 1.5 hrs. to 320 g. trichlorododecylsilane, the mixture refluxed at  $46-50^\circ$  overnight, the mixture cooled, the solids removed, and the solvents removed gave 20.5 g. dodecane,  $b_{0.7-1.3} 75-105^\circ$ . Further distillation gave three fractions: 140 g.,  $b_{0.1}$

UNSYMMETRICALLY-SUBSTITUTED SILOXANYL FERROCENES, U. S. Patent 3,036,105, 22 May 1962, Applied 24 August 1960, 5 pp.

The title compounds are high boiling stable substances, good for high temperature hydraulic fluids and lubricants. A solution of BuLi was added dropwise during 1 hr. to a stirred solution of 397 g. cyclopentadiene in 3600 cc. anhydrous Et<sub>2</sub>O under N in an ice-bath. After the mixture was stirred 1.5 hrs. without an ice-bath, a mixture of 1460 ml. Me<sub>2</sub>SiCl<sub>2</sub> and 1500 cc. Et<sub>2</sub>O was added, and the mixture refluxed 17 hrs. The volume of the mixture was then reduced by vacuum distillation and the mixture was filtered and washed with Et<sub>2</sub>O. After removal of volatile material from the filtrate under vacuum, distillation of the residue gave 657 g. cyclopentadienyldimethylchlorosilane (I), b<sub>7.0-4.5</sub> 37-40°. A solution of 63.4 g. I in 500 cc. Et<sub>2</sub>O was stirred under N in an ice-bath. Pyridine (31.6 g.) was added in one portion followed by the dropwise addition of 18.4 g. EtOH during 15 min. The mixture was stirred overnight, filtered, the solid washed with Et<sub>2</sub>O, and the filtrate evaporated in vacuo. The residue was distilled and the distillate, b<sub>26</sub> 36-50°, fractionated to give 50.0 g. cyclopentadienyldimethyl ethoxysilane (II). An isopropylmagnesium chloride solution was prepared by the dropwise addition of 100 cc. isopropyl chloride to 27 g. Mg in 250 cc. Et<sub>2</sub>O. After the reaction had been initiated by a mixture of 3 cc. isopropyl bromide and 25 cc. isopropyl chloride, a solution of 168 g. II in 1 l. tetrahydrofuran was stirred under N in an ice-bath until cold and the isopropylmagnesium chloride solution was then added during 15 min. After the mixture had been stirred an additional hour in the ice-bath a FeCl<sub>2</sub> solution, prepared from 54.2 g. FeCl<sub>3</sub> and 9.4 g. Fe powder in 200 cc. tetrahydrofuran, was added in four portions. The ice-bath was removed and the mixture stirred overnight. Solvent was removed by evaporation in vacuo and the residue was extracted with petr. ether. Evaporation of the extract and subsequent distillation gave 121 g. 1,1'-bis(dimethylethoxysilyl)ferrocene (III), b<sub>0.4</sub> 131-2°, m. 14.5-17°. To a mixture of 118.4 g. III, 250 cc. dioxane, and 10 cc. H<sub>2</sub>O was added 2.5 cc. concentrated HCl. The solution was allowed to stand 48 hrs. and the solvent removed by evaporation under vacuum. Extraction of the residue with a little MeOH left 73.8 g. 1,3-(1,1'-ferrocenyl-ene) tetramethyldisiloxane (V), m. 86-8°. Evaporation of

the extract and recrystallization of the residue from isopropyl alcohol furnished an additional 11.0 g. V, m. 86-7°. A solution of PhBr in 30 cc. Et<sub>2</sub>O was added to 1 g. Li slices in 50 cc. Et<sub>2</sub>O during 0.5 hr. with an additional 1-hr. reflux. The PhLi solution was added to 20 g. V in 250 cc. Et<sub>2</sub>O and the mixture was refluxed overnight. To this mixture was added 3.0 g. MeSiCl<sub>2</sub> in 50 cc. Et<sub>2</sub>O. The mixture was stirred overnight at room temperature, filtered, and the solvent removed from the filtrate in vacuo. The residue was extracted with petr. ether and the extract evaporated. Distillation of residue gave a fraction, b<sub>0.2</sub> 80-100°, from which 2.6 g. V recovered by recrystallization from MeOH. A second fraction, b<sub>0.14</sub> 270-6°, was shown by analysis to be tris[(1-phenyldimethylsilylferrocenyl)dimethylsiloxy] methylsilane, b<sub>0.06</sub> 273-80°. The following compounds were also prepared: 1,1'-bis[3-(1-phenyldimethylsilylferrocenyl)-1,1,3,3,-tetramethyldisiloxanyl] ferrocene, b<sub>0.08</sub> 310-20°; 1-trimethylsilyl-1'-(3-phenyl-1,1,3,3-tetramethyldisiloxanyl) ferrocene; 1,5-bis(1-trimethylsilylferrocenyl)-1,1,3,3,5,5-hexamethyltrisiloxane; 1,3-bis[1-(3-phenyltetramethyldisiloxanyl)ferrocenyl] tetramethyldisiloxane, b<sub>0.025</sub> 283-90°, n<sub>D</sub><sup>25</sup> 1.5572; 1-phenyldimethylsilyl-1'-(3-phenyl-1,1,-3,3-tetramethyldisiloxanyl) ferrocene, b<sub>0.03</sub> 200-8°, n<sub>D</sub><sup>25</sup> 1.5740; 1,5-bis(1'-phenyldimethylsilyl-1-ferrocenyl)-1,1-3,3,5,5-hexamethyltrisiloxane, b<sub>0.03</sub> 283-5°, n<sub>D</sub><sup>25</sup> 1.5791.

310. Schaaf, R. L., Lenk, C. T., and Rosenberg, H.,  
 SYMMETRICAL SILOXANYLFERROCENES. U. S. Patent  
 3,010,982, 28 November 1961, Applied 7 April 1960, 3 pp.

R = cyclopentadienyl in this abstract. The title compounds were prepared by treating trisubstituted silylcyclopentadienes with BuLi and then with FeCl<sub>2</sub>. Thus, six moles RH in Et<sub>2</sub>O at 0° under N treated with six moles of BuLi, stirred 1.5 hrs. at room temperature, the mixture treated with 12 moles Me<sub>2</sub>SiCl<sub>2</sub> in dry Et<sub>2</sub>O, stirred an additional 17 hrs., the Et<sub>2</sub>O removed in vacuo, and the solution filtered and fractionated gave 657 g. RMe<sub>2</sub>SiCl (I), b<sub>7-4.5</sub> 37-40°. PhMe<sub>2</sub>SiONa (43.5 g.), in dry Et<sub>2</sub>O added to 39.7 g. I in Et<sub>2</sub>O at 0° under N, the mixture stirred 12 hrs., filtered, evaporated in vacuo, and distilled gave 55 g. RMe<sub>2</sub>SiOSiMe<sub>2</sub>Ph (II), b<sub>0.05-0.03</sub> 83.6°. BuLi and II (0.1 mole each) in Et<sub>2</sub>O under N stirred and refluxed 18 hrs., the mixture treated with fresh FeCl<sub>2</sub> (0.033 moles) in dry tetrahydrofuran, the Et<sub>2</sub>O distilled, the solution refluxed 15 hrs., evaporated in vacuo, extracted with

petr. ether, and the extract fractionated gave 17.6 g. 1,1'-bis(3-phenyltetramethyldisiloxanyl)ferrocene,  $b_{0.03}$  200-5°, m. 18-19.5°, pour point -31°, viscosity 21.7 cp., wt. loss on heating at 366° 10 hrs. 0.5 percent. Also prepared were [compound, b.p. /mm., pour point, percent wt. loss on heating 10 hrs. at 366°, viscosity (cp.) before, after heating]: 1,1'-bis(5-phenylhexamethyltrisiloxanyl)ferrocene, 220-3°/0.15, -40°, 0.4, 16.8, 17.8; 1,1'-bis(7-phenyloctamethyltetrasiloxanyl)ferrocene, 245-55°/0.04, -57°, 2.6, 17.2, 16.8; 1,1'-bis(3-phenyltetramethyldisiloxanyl)ferrocene, 205-15°/0.07, -22°, 1.1, 30.8, 31; 1,1'-bis(3,3,3-triphenyl-1,1-dimethyldisiloxanyl)ferrocene, m. 148.5-50(Me<sub>2</sub>CO), -, 1.0, -, -; 1,1'-bis(pentamethyldisiloxanyl)ferrocene, 107.10°/0.01, -, -, -, -. All compounds decomposed slowly above 850°F. Wide liquid range, good thermal stability, and favorable electrical properties make the title compounds useful as hydraulic fluids, greases, lubricants, and dielectrics.

311. Wilkus, E. V. and Berger, A.,  
ORGANOBIS(SILYL FERROCENES), French Patent 1,398,255  
(Cl. C 07f), 7 May 1965, U. S. Applied 27 May 1963, 11 pp.

[Me<sub>3</sub>SiRY(C<sub>5</sub>H<sub>4</sub>FeC<sub>5</sub>H<sub>4</sub>)Y<sup>1</sup>]<sub>2</sub>A (I) where R is CH<sub>2</sub>CH<sub>2</sub> or C<sub>6</sub>H<sub>4</sub>, Y = Y<sup>1</sup> = C=O or CH<sub>2</sub> and A is C<sub>6</sub>H<sub>4</sub> or (CH<sub>2</sub>)<sub>4</sub>; were prepared by treating a silylorganoferrocene Me<sub>3</sub>SiRY(C<sub>5</sub>H<sub>4</sub>-FeC<sub>5</sub>H<sub>4</sub>) (II) with a dicarboxylic acid halide A(COX)<sub>2</sub> (III) where X is a halogen at -25° to 100° in the presence of a Friedel-Crafts catalyst. II were prepared by acylating ferrocene with a silyl carboxylic acid halide Me<sub>3</sub>SiRCOX (IV) also in the presence of a Friedel-Crafts catalyst. In an example, 2.74 parts AlCl<sub>3</sub> was added slowly with shaking to a mixture of three parts β-trimethylsilylpropionyl ferrocene, 0.93 parts terephthaloyl chloride, and 20 parts CH<sub>2</sub>Cl<sub>2</sub> and the mixture shaken 32 hrs. When the evolution ceased, the mixture was hydrolyzed by adding a mixture of 75 parts ice-water and nine parts concentrated HCl and then 60 parts CHCl<sub>3</sub>, the mixture allowed to stand several days, neutralized with 5 percent KOH solution dried over alumina, and evaporated. The dark red solid was taken up in Et<sub>2</sub>O and CH<sub>2</sub>Cl<sub>2</sub>, and the solution subjected to a chromatographic separation on a neutral alumina column containing 177 μ particles in the presence of n-hexane to yield 22 percent I (R = CH<sub>2</sub>CH<sub>2</sub>, Y = Y<sup>1</sup> = >C:O and A = p-C<sub>6</sub>H<sub>4</sub>), m. 147-8°. Compounds

similarly prepared were I [ R = p-C<sub>6</sub>H<sub>4</sub>, Y = Y' = C:O and A = (CH<sub>2</sub>)<sub>4</sub> ] and [ R = CH<sub>2</sub>CH<sub>2</sub>, Y = Y' = CH<sub>2</sub> and A = p-C<sub>6</sub>H<sub>4</sub> ] I may be used as an absorber of uv radiation, antioxidants, anti-shock agents, and as agents favoring the formation of complexes for metal ions.

312. Wu, G.,  
ORGANOSILICON DERIVATIVES OF DICYCLOPENTADIENYL  
IRON (Foreign Title Not Available), Translated into English  
from Chinese from Huaxue Tongbao by the Air Force Systems  
Command, Foreign Technology Division, Wright-Patterson  
Air Force Base, Ohio, 7 July 1965, Report No. FtD-TT-64-  
1345/1+2+3+4, AD-618 007, N65-33007 (No. 5, 1963, pp.  
293-301).

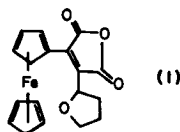
A variety of organosilicon derivatives of dicyclopentadienyl iron are described. The two basic methods of derivation constituted introduction of a silanyl substituting group to the nucleus of dicyclopentadienyl iron with the formation of mono- and di-substituted derivatives, or to obtain the silicon containing derivatives of dicyclopentadiene first, then metallizing them with RMgX, RNa, and RLi and subsequent condensation with FeCl<sub>2</sub>.

313. Wu, K.,  
ORGANOSILICON DERIVATIVES OF FERROCENE, Hau  
Hsueh T'ung Pao, No. 5, 1963, pp. 293-301.

A review of the synthetic methods for the title compounds, especially for the different types of ferrocene-siloxanes. 21 references are given.

314. Bozak, R. E.,  
FREE-RADICAL REACTION OF FERROCENE WITH  
MALEIC ANHYDRIDE, Journal of Organic Chemistry, Vol.  
31, No. 2, 1966, pp. 610-611.

Ferrocene and maleic anhydride in tetrahydrofuran or dioxane in the presence of a trace of  $\text{H}_2\text{O}_2$  afforded a new compound (I). Structure of I was determined by infrared, ultraviolet, and nuclear magnetic resonance analysis.



315. Egger, H. and Schloegel, K.,  
FERROCENE DERIVATIVES. XXIII. FERROCENYLACETYLENES. 4. PREPARATION AND LIGHT-ABSORPTION OF FERROCENYLTHIOPHENES AND FERROCENYLACETYLENES, Monatsheft Chemie, Vol. 95, No. 6, 1964, pp. 1750-1758 (In German, cf. CA 59, 7557f, 61, 14708h, 16091g).

Refer to item No. 213 for abstract.

316. Fitzgerald, W. P., Jr.,  
THE CHEMISTRY OF  $\alpha$ -SUBSTITUTED FERROCENE  
DERIVATIVES, Dissertation Abstract, Vol. 24, No. 7,  
1964, p. 2687 (University Microfilms).

Vinylferrocene and  $\alpha$ -methylvinylferrocene have been prepared in good yield and high purity by newly developed pyrolytic-dehydration procedures. By addition of halogen-containing species to these olefins,  $\alpha$ -chloro- and  $\alpha$ -bromo-ethylferrocene,  $\alpha$ ,  $\beta$ -dibromoethylferrocene, ferrocenylisopropyl chloride and 2, 2-dichlorocyclopropylferrocene have been synthesized and characterized. These halides have been converted to 1-ferrocenylethyl azide, 1-ferrocenylethanol, ferrocenylacetylene, tert-butylferrocene and cyclopropylferrocene, respectively. Ferrocenylacetylene was converted to  $\alpha$ ,  $\alpha$ -dichloroethylferrocene,  $\alpha$ -chlorovinylferrocene and ferrocenylpropionic acid. Hydroboration of vinylferrocene provided a facile route to

2-ferrocenylethanol. Various attempts to convert this carbinol to open-chain beta-haloferrocene were unsuccessful. All the above ferrocenylalkylhalides except the cyclopropyl compound showed limited thermal stability.

The diversified synthetic utility of the alpha-haloferrocenes has been further demonstrated. Treatment of alpha-chloroethylferrocenes with such nucleophiles as methyllithium, n-amylsodium, lithium aluminum hydride, sodium methoxide and phenoxide at  $-78^{\circ}$  gave in all cases a high preponderance of the corresponding substitution product, with little or no elimination product. Similar effects were noted in the reactions of ferrocenylisopropyl chloride with lithium aluminum hydride and sodium methoxide. Several of these reactions were observed to give higher elimination/substitution ratios with increased temperature, but the product ratios at  $-78^{\circ}$  were solvent-independent. Kinetic data and other chemical evidence has been obtained in support of an SN-1 mechanism, involving the alpha-ferrocenylalkylcarbonium ion, for these substitutions. Treatment of alpha-chloroethylferrocene with sodium and magnesium gave no evidence for an organometallic intermediate.

The triferrocenylmethyl system has been synthesized, in the form of triferrocenylcarbinol, by treatment of diferrocenylketone and also methyl ferrocenoate with ferrocenyllithium. Both reactions produced significant amounts of biferrocenyl as well, and the latter reaction also gave some diferrocenylketone. The organometallic was prepared from the corresponding mercuric halide by transmetalation. Mixed hydride reduction of triferrocenylcarbinol gave the parent hydrocarbon, triferrocenylmethane. Facile methanolysis of the carbinol produced triferrocenylmethyl methyl ether. This ether was cleaved by sodium-potassium alloy to give triferrocenylmethane also, although no stable carbanion was involved in this cleavage. These new, multiferoecenoid compounds have been fully characterized. Reactions of triferrocenylcarbinol with hydrogen chloride, aluminum chloride, as well as with ferrocene and anisole have been carried out.

To examine the possibility of alpha-carbanion stabilization by ferrocene, the following ethers were cleaved by sodium-potassium alloy at  $25^{\circ}$ : methoxymethylferrocene, alpha-methoxyethylferrocene, ferrocenylisopropyl methyl ether, alpha-phenoxyethylferrocene, alpha-methoxybenzylferrocene and di-ferrocenylmethyl ether. The first two members of this series were also cleaved by lithium in tetrahydrofuran. In all cases cleavage of the alpha-alkyloxygen bond occurred, with subsequent hydrogen-abstraction to

form the corresponding alkylferrocene. In all cases, the hydrocarbon formation was demonstrated, by vapor-phase chromatography, to occur prior to or in the absence of hydrolysis. In no case was a ferrocenoid acidic product formed upon carbonation. When the cleavages were carried out in the presence of a halosilane, the corresponding alpha-ferrocenylalkylsilane was obtained in good yield. The comparative rates of cleavage, as well as dimeric by-products observed, with variation in the ether structure, have been examined in view of possible mechanistic consequences.

317. Hata, K., Motoyama, I., and Watanabe, H.,  
THE SYNTHESIS OF GLYCIDYLFERROCENES, Bulletin  
Chemical Society of Japan, Vol. 36, No. 12, 1963, pp.  
1698-1699.

Ferrocene (I) was converted to its Li derivative by treatment with BuLi in anhydrous Et<sub>2</sub>O under N. An Et<sub>2</sub>O solution of epichlorohydrin was added slowly at -50° and the mixture poured into H<sub>2</sub>O. The organic layer was concentrated, I filtered off, and the residue distilled to give dark red chlorohydrin (II), b<sub>0.8-0.9</sub> 156-8°. An Et<sub>2</sub>O solution of crude II was cooled to 0° and aqueous KOH added with stirring. After addition of more Et<sub>2</sub>O and H<sub>2</sub>O crude glycidylferrocene (III) was obtained from the organic layer. Pure III b<sub>0.1-0.2</sub> 111-15°, n<sub>D</sub><sup>20</sup> 1.6093 (dark red). The yield was 13 percent from I. From the residues of the distillation a small quantity of diglycidylferrocene (IV) was obtained. The distillation residue was treated with HCl-dioxane and the bis (chlorohydrin) purified by chromatography over Al<sub>2</sub>O<sub>3</sub> (C<sub>6</sub>H<sub>6</sub>) and then converted to IV, which was purified on Al<sub>2</sub>O<sub>3</sub> (1:1 C<sub>6</sub>H<sub>6</sub>:Et<sub>2</sub>O). IV was a dark red liquid. The yield from I was 0.3 percent.

318. Koestler, R. C.,  
THE PREPARATION OF HETEROANNULAR SUBSTITUTED  
FERROCENES FROM FULVENES AND FULVENOID  
COMPOUNDS, Dissertation Abstract, Vol. 22, 1962,  
pp. 3401-3402 (University Microfilms).

A new method for the preparation of heteroannular disubstituted ferrocenes from fulvenes has been developed. Either phenyllithium or lithium aluminum hydride has been found to add to the exo-double bond of fulvenes, forming



substituted cyclopentadienide ions which yield heteroannular disubstituted ferrocenes on treatment with anhydrous ferrous chloride. 1, 1'-Dibenzylhydrylferrocene, 1, 1'-dicumenylferrocene, and 1, 1'-diisopropylferrocene have been prepared by this method.

A convenient and improved method has been developed for the preparation of ferrocene in 90 percent yield from cyclopentadiene and anhydrous ferrous chloride, using sodium ethoxide as the base and absolute ethanol as the solvent. This reaction proceeds also with commercial hydrated ferrous chloride, with a decrease in yield to 30 percent.

The synthesis of some symmetrical heteroannular tetrasubstituted ferrocenes of known substitution patterns has been accomplished. The action of lithium aluminum hydride on 1, 2-dibenzoylcyclopentadiene followed by treatment with ferrous chloride resulted in the formation of 1, 1', 2, 2'-tetrabenzylferrocene. The generality of the reaction was established by the synthesis of the following compounds by the same method: 1, 1', 2, 2'-tetrakis (p-chlorobenzyl) ferrocene, 1, 1', 2, 2'-tetrakis (p-bromobenzyl) ferrocene, 1, 1', 2, 2'-tetrakis (p-methylbenzyl) ferrocene, 1, 1', 2, 2'-tetrakis (p-fluorobenzyl) ferrocene, 1, 1', 2, 2'-tetrakis (m-bromobenzyl) ferrocene, and 1, 1', 2, 2'-tetrakis (o-chlorobenzyl) ferrocene.

319. Hallam, B. F., Pauson, P. L., Broadhead, G. D., and Osgerby, J. M.,

FERROCENE DERIVATIVES. IV. INDENYL- AND TETRAHYDROINDENYLIRON CARBONYLS. V. FERROCENEALDEHYDE. VI. DL-FERROCENYLALANINE, Journal of Chemical Society, 1958, pp. 646-660 (CA 51, 2607f).

The structures of spiro [2.4] hepta-1, 3-diene (I) and spiro [4.4] nona-1, 3-diene (II) were confirmed. Both I and II rearrange during their reactions with  $\text{Fe}(\text{CO})_5$  (III). II yields bistetrahydroindenyliron tetracarbonyl (IV), which is converted by pyrolysis to bistetrahydroindenyliron (V). Indene (VI) reacts with III to give diindenyliron tetracarbonyl (VII) which was reduced to the same V. Cyclopentadiene (50g.) treated during 0.5 hr. under reflux with 35 g. Na in 1500 ml. liquid  $\text{NH}_3$ , 144 g.  $(\text{CH}_2\text{Br})_2$  added during 40 min.,

the mixture stirred 1.5 hrs., treated with  $\text{Et}_2\text{O}$  and  $\text{H}_2\text{O}$ , and the  $\text{Et}_2\text{O}$  washed and evaporated gave 13.2 g. I,  $b_{0.3}$  45-7°,  $n_D^{20}$  1.5070. I (0.35 g.) reacted exothermally with 0.37 g. maleic anhydride in 4 ml.  $\text{C}_6\text{H}_6$ , it was then allowed to stand 1 hr. at room temperature and the solution evaporated to give 0.65 g. adduct, m. 97-8° ( $\text{Et}_2\text{O}$ -ligroine). I (2.76 g.) in 50 ml.  $\text{EtOAc}$  treated during 3.5 hrs. at -78° with passage of 3.3 percent  $\text{O}_3$  at 350 ml. O per min., 75 ml.  $\text{AcOH}$  added, the solution evaporated to 20 ml. volume, added to 20 ml.  $\text{H}_2\text{O}_2$ , 0.75 ml. concentrated  $\text{H}_2\text{SO}_4$ , and 30 ml.  $\text{H}_2\text{O}$ , cautiously warmed to 40°, kept at this temperature 1 hr., left 36 hrs. at room temperature, and the solution evaporated acidified with dilute  $\text{HCl}$ , and continuously extracted 24 hrs. with  $\text{Et}_2\text{O}$  to give 1.33 g. 1, 1-cyclopropanedicarboxylic acid, m. 134-6° ( $\text{CHCl}_3$ -ligroine). Cyclopentadiene (28 g.), 80 g.  $(\text{CH}_2)_4\text{Br}_2$ , and 500 ml. liquid  $\text{NH}_3$  treated with 20 g. Na as above gave 5.7 g. II,  $b_{22}$  44-6°,  $n_D^{20}$  1.4817. II (0.20 g.) reacted exothermally with 0.163 g. maleic anhydride in  $\text{C}_6\text{H}_6$ , giving 0.33 g. of the adduct, m. 100-1°. Hydrolysis of 0.26 g. of the adduct 1 hr with 20 ml. 2N  $\text{NaOH}$  gave 0.277 g. corresponding dicarboxylic acid, m. 180° (decomposition). A pure sample of this acid was reconverted into the anhydride by refluxing 1.5 hrs. with 2 ml.  $\text{AcCl}$ ; it gave 83 mg. product identical with the original adduct. II (2.4 g.) ozonized 2.5 hrs. and treated with  $\text{H}_2\text{O}_2$ , concentrated  $\text{H}_2\text{SO}_4$ , and  $\text{H}_2\text{O}$  gave after separation 125 mg. nonketonic oil not further investigated and 0.31 g. 1, 1'-cyclopentanedicarboxylic acid (VIII), m. 185° (decomposition).  $\text{KMnO}_4$  (12.5 g.) added portionwise during 1 hr. to 1.2 g. II and 0.5 g.  $\text{NaHCO}_3$  in 50 ml.  $\text{Me}_2\text{CO}$ , the mixture stirred overnight, acidified,  $\text{SO}_2$  passed in, and the solution then extracted 24 hrs. with  $\text{Et}_2\text{O}$  gave 0.28 g. neutral oil and 0.485 g. VIII, m. 186° (decomposition). II (4 g.) heated 24 hrs. at 130° in a sealed tube and the solvent evaporated gave 3.65 g. liquid which did not react with maleic anhydride, and distillation of a portion at 100-5°/19 mm. yielded 0.28 g. product. The remainder (1.65 g.) distilled at 110-20°/0.01 mm. gave a molecular weight calculated for the dimer. I (13 g.) and 28 g. III heated 36 hrs. at 140° under  $\text{CO}_2$  in an autoclave, and the product extracted with  $\text{Me}_2\text{CO}$  and evaporated gave unchanged III. The residual oil was dissolved in  $\text{C}_6\text{H}_6$ , chromatographed on  $\text{Al}_2\text{O}_3$ , and the main purple band eluted with 3:2  $\text{C}_6\text{H}_6$ -ligroine; this on evaporation gave 216 mg. bis (ethylcyclopentadienyl) diiron tetracarbonyl, m. 61-2°

(decomposition). II (8 g.) and 12 g. III heated 25 hrs. at 130° under CO<sub>2</sub> in an autoclave and the product chromatographed on Al<sub>2</sub>O<sub>3</sub> gave 6 g. crude IV, m. 148° (decomposition) (ligroine), 1951 and 1754 cm.<sup>-1</sup> (KBr disc.). IV was recovered unchanged after its MeOH solution was stirred with H and PtO<sub>2</sub>. IV (0.5 g.) heated a few minutes over a free flame gave an oil which was chromatographed on Al<sub>2</sub>O<sub>3</sub> and, when distilled at 130°/0.05 mm., gave V. VII (0.1 g.) in 25 ml. alcohol stirred with 150 ml. PtO<sub>2</sub> and H until the uptake ceased, the mixture worked up gave IV. Freshly distilled VI (12 g.) and 20 g. III heated 24 hrs. at 130° in an autoclave and the product separated gave 4.6 g. VII, brownish purple crystals, m. 198° (decomposition),  $\nu$  1951 and 1790 cm.<sup>-1</sup>

## V

Ferrocene (I) is much more reactive toward Friedel-Crafts acylation than either C<sub>6</sub>H<sub>6</sub> or anisole (II). The first acyl substituent deactivates even the unsubstituted ring. The high reactivity of I is utilized in its conversion into its monoaldehyde (III) by the HCONMePh (IV) method. III shows the typical properties of an aromatic aldehyde; it undergoes the Cannizzaro reaction, was converted via its oxime (V) into ferrocenyl cyanide (VI), and was condensed with CH<sub>2</sub>(CO<sub>2</sub>H)<sub>2</sub> (VII), with  $\alpha$ -picoline MeI salt (VIII), and, in a mixed benzoin condensation, with BzH. An alternative preparation of III is also described. The reagent used in all experiments was prepared by dissolving a known weight of AcCl in dry alcohol-free CHCl<sub>3</sub>, keeping the mixture 2 hrs. in contact with AlCl<sub>3</sub>, and then adding H<sub>2</sub>O; gravimetric estimation of Al by the oxine method indicated that 90 percent of the AlCl<sub>3</sub> required to form a 1:1 AcCl:AlCl<sub>3</sub> complex (IX) was dissolved. IX was added during 15-20 min. to a stirred solution of I in CHCl<sub>3</sub> under N at 0°, the mixture stirred the specified time, ice added, with sufficient Ti<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> to reduce any ferricinium salt, the organic layer separated, dried, evaporated, and the residue chromatographed on Al<sub>2</sub>O<sub>3</sub> with C<sub>6</sub>H<sub>6</sub>. The following results were obtained (moles of I, AcCl in moles, time in hrs., percent I recovered, percent acetylferrocene (X), percent diacetylferrocene (XI), and total percent I accounted for given): 0.013, 0.013, 0.5, 53, 47, trace, 95; 0.011, 0.011, 0.5, 50, 47, trace, 92; 0.018, 0.018, 1.5, 44, 54, trace, 92; 0.016, 0.05, 1, 0, 3, 73, 76; 0.018, 0.09, 1.5, 6, 15, 71, 92; 0.02, 0.018, 1.5, 56, 9.7, 54, 89; 0.016, 0.016, 5, 55, 13, 19, 85.

Similar acetylations of X required the addition of solid  $\text{AlCl}_3$  and then gave 85 percent XI and 10 percent unchanged X after 2 hrs. Without free  $\text{AlCl}_3$  only 1 percent XI was formed, probably owing to the formation of a complex by X which therefore abstracted the  $\text{AlCl}_3$  from IX. I (3 g.) and 1.64 g.  $\text{Ac}_2\text{O}$  in  $\text{CHCl}_3$  treated 2 hrs. at  $0^\circ$  with  $\text{BF}_3$  and the solution left 4 hrs. at  $0^\circ$  and worked up as before gave 0.36 g. I and 2.36 g. X. Attempted competitive acetylations of I and  $\text{C}_6\text{H}_6$ , II, or  $\text{PhOH}$  were carried out as above (amount in moles of I,  $\text{AcCl}$ , and third component, and percent yield given): 0.02, 0.014,  $\text{C}_6\text{H}_6$ , 0.02, 50; 0.018, 0.012, II, 0.018, 35; 0.018, 0.016, II, 0.18, 47; 0.016, 0.016,  $\text{PhOH}$ , 0.016, 9. In the last experiment, 91 percent I was recovered. No other ketonic products were detected in any of these experiments. IV (4.4 g.) and 5 g.  $\text{POCl}_3$  left 1 hr. at room temperature, 2.99 g. I added portionwise during 0.5 hr. with cooling, the mixture left 72 hrs., ice  $\text{H}_2\text{O}$  added, the mixture left some hrs. to effect decomposition, extracted with  $\text{CHCl}_3$ , dried, evaporated, and a  $\text{C}_6\text{H}_6$  solution of the residue chromatographed on  $\text{Al}_2\text{O}_3$  gave 0.125 g. unchanged I and IV. The chief red band on elution gave 2.56 g. III, m.  $121^\circ$  (aqueous alcohol-ligroine), sublimed at  $70^\circ/0.01$  mm.,  $\lambda$  226, 271, 344, and 461  $\text{m}\mu$ ,  $\log \epsilon$  3.24, 3.88, 3.17, and 2.78. Ferrocenylmethyltrimethylammonium iodide (4.5 g.) in 22 ml.  $\text{AcOH}$  refluxed 1 min. with 5.7 g. hexamethylenetetramine gave 0.92 g. III. V was isolated in two distinct forms, depending on the method of preparation. Recrystallization of each form appeared to cause partial conversion into the other. The  $\alpha$ -form was tentatively assigned the  $\text{syn}$ - and the  $\beta$ -form the anti-configuration. The  $\text{syn}$ -form had the lower m.p. was more acidic, and formed under basic reaction conditions, whereas the anti-isomer formed in acidic medium. The  $\text{syn}$ -form m.  $96-9^\circ$  (ligroine). It was readily soluble in 2N  $\text{NaOH}$ . To recover V from such solutions it was necessary to acidify them carefully at low temperature, or, preferably, with solid  $\text{CO}_2$ , to avoid partial hydrolysis to III.  $\text{H}_2\text{NOH} \cdot \text{HCl}$  (0.7 g.) and 1 g.  $\text{NaOAc}$  in 4 ml.  $\text{H}_2\text{O}$  refluxed 2-3 hrs. with 1 g. III in 6 ml. alcohol, cooled, extracted with  $\text{Et}_2\text{O}$ , the  $\text{Et}_2\text{O}$  washed with 2N  $\text{NaOH}$ , and the aqueous layer acidified gave a small amount of oxime. The  $\text{Et}_2\text{O}$  layer gave 0.5 g.  $\beta$ -form of V, m.  $155-7^\circ$ , lowered to  $145-6^\circ$  ( $\text{C}_6\text{H}_6$ ) by 4 recrystallizations. III (1.5 g.) and 0.7 g.  $\text{H}_2\text{NOH} \cdot \text{HCl}$  in 10 ml. alcohol refluxed 2 hrs. under N, cooled, 1.34 g. of the black oxime  $\text{HCl}$  salt removed, this

suspended in Et<sub>2</sub>O, the free oxime liberated by shaking with Na<sub>2</sub>CO<sub>3</sub>, evaporation and crystallization gave crude α-form of V, m. 150-2°. V (β-form, 0.15 g.) and 0.17 g. dicyclohexylcarbodiimide removed on cooling, the C<sub>6</sub>H<sub>6</sub> solution extracted with dilute NaOH (which removed 15 mg. unchanged V), the C<sub>6</sub>H<sub>6</sub> evaporated, and the product crystallization gave 97 mg. VI. Under identical conditions the α-form of V gave 50 percent VI and 14 mg. unchanged material. V (either form) (1 g.) and 10 ml. Ac<sub>2</sub>O warmed 20 min., then refluxed 20 min., the solution poured into 30 ml. H<sub>2</sub>O, extracted with CHCl<sub>3</sub>, and the residue chromatographed on Al<sub>2</sub>O<sub>3</sub> gave VI, plates, m. 107-8° (ligroine),  $\nu$  2242 cm.<sup>-1</sup> V (mixed isomers) (1 g.) in 25 ml. Et<sub>2</sub>O treated 2 hrs. with 1.5 g. PCl<sub>5</sub> gave 25 percent VI. V (mixed isomers) (1.8 g.) in 40 ml. alcohol shaken 48 hrs. with 2 g. Raney Ni and similarly worked up gave 6 percent VI, together with 30 percent unchanged V and a trace of free III. I (6 g.), 8.4 g. anhydrous AlCl<sub>3</sub>, and CS<sub>2</sub> treated at 0° with 4.24 g. CNBr, held 4 hrs., and refluxed 1 hr. gave 4 g. I with a trace of VI. All attempts to improve the yield failed. III (2 g.) refluxed in C<sub>6</sub>H<sub>6</sub>, 1 ml. (CH<sub>2</sub>OH)<sub>2</sub>, and a trace of p-MeC<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>H overnight through a Soxhlet apparatus filled with CaSO<sub>4</sub>, evaporated, and the residue chromatographed with cyclohexene as solvent gave 2 g. 2-ferrocenyl-1,3-dioxolane, m. 81-2° (ligroine). III (0.26 g.) in 5 ml. MeOH rapidly reduced with 0.061 g. NaBH<sub>4</sub> gave 0.216 g. ferrocenylmethanol (XII), m. 76° (H<sub>2</sub>O). III (0.5 g.) refluxed 3 hrs. with 10 ml. 50 percent alcohol KOH, diluted, and extracted with Et<sub>2</sub>O gave 0.12 g. XII. Acidification of the alkaline layer gave 0.025 g. ferrocenecarboxylic acid, m. 210° (decomposition). III (1 g.) and 1 ml. 40 percent HCHO in 10 ml. MeOH heated to 65°, treated with 2.66 g. KOH in 2 ml. H<sub>2</sub>O refluxed 3 hrs., and the crude product chromatographed gave 0.045 g. XII and 0.5 g. unchanged III. III (0.5 g.), 0.5 g. VII, and 10 drops piperidine in 12 ml. C<sub>5</sub>H<sub>5</sub>N refluxed 2 hrs., the solution diluted with H<sub>2</sub>O, extracted with CHCl<sub>3</sub>, the CHCl<sub>3</sub> extract washed with dilute HCl and with 2N NaOH, and the aqueous layer acidified gave 0.4 g. β-ferrocenylacrylic acid, red prisms, m. 186-7° (decomposition) (C<sub>6</sub>H<sub>6</sub>). III (0.3 g.), 0.3 g. VIII, and 1 ml. piperidine in 20 ml. MeOH refluxed 3 hrs. under N gave 1-ferrocenyl-2-(2-pyridyl) ethylene methiodide, prisms, which could not be satisfactorily recrystallized. III (1.07 g.), 0.53 g. BzH, 15 ml. alcohol, and 0.5 g. KCN in 1 ml. H<sub>2</sub>O refluxed 1.5

hrs., diluted with H<sub>2</sub>O, and refrigerated 2 hrs. gave 0.37 g. mandeloylferrocene, m. 148-9° (aqueous alcohol).

## VI

Syntheses of DL-ferrocenylalanine (I) from ferrocene-carboxaldehyde (II) by the azlactone method, and, more efficiently, from (ferrocenylmethyl) trimethylammonium iodide (III) via (ferrocenylmethyl) formamidomalonic ester (IV) are described. IV was converted into ferrocenylacetic (V) and -propionic acid (VI). II (1 g.), 1 g. hippuric acid, and 0.4 g. anhydrous NaOAc in 4 ml. Ac<sub>2</sub>O refluxed 5 min. under N, and the solution heated 1.5 hrs. on a steam bath, cooled, diluted with 6 ml. MeOH, and refrigerated overnight gave 0.964 g. azlactone (VII), m. 188°. No crystalline azlactone could be obtained when acetylglycine was used instead of hippuric acid. VII (2 g.) refluxed 15 min. with 0.6 g. NaOH in 25 ml. 50 percent aqueous alcohol, cooled, acidified, and the solids collected gave 2 g. α-benzanido-β-ferrocenylacrylic acid (VIII), rods, m. 218-19°. VIII (1 g.) in 40 ml. alcohol refluxed 1 hr. with 4 g. Na, cooled, poured into H<sub>2</sub>O, filtered, and the filtrate acidified gave β-ferrocenyl-α-(cyclohexylformamido) propionic acid (IX), plates, m. 222-3° (decomposition). IX was obtained in a 38 percent yield from VII similarly reduced. Ferrocene (X) (10 g.) refluxed 8 hrs. with 8 g. methylenebisdimethylene, 8 g. H<sub>3</sub>PO<sub>4</sub>, and 80 ml. AcOH under N, cooled, poured into H<sub>2</sub>O, extracted with Et<sub>2</sub>O, and the aqueous layer made alkaline evaporated, and crystallized gave III, yellow solid, m. 220° (decomposition). X (0.9 g.) refluxed 8 hrs. with 1.8 g. methylenebispiperidine, 1 g. H<sub>3</sub>PO<sub>4</sub>, and 10 ml. AcOH gave 0.94 g. piperidinomethylferrocene, leaflets, m. 84-5.5° (ligroine). III (3.9 g.) in 10 ml. alcohol refluxed 2 hrs. gave 0.92 g. unchanged III and 0.83 g. ferrocenylacetonitrile (XI), m. 85° (ligroine). XI (0.105 g.) refluxed 1.5 hrs. with 1 g. NaOH in 9 ml. alcohol and 7 ml. H<sub>2</sub>O gave 0.07 g. V, semi-solid mass at 1409 and final m. 161°. Acetylferrocene (1 g.), 0.2 g. S, and 0.6 g. morpholine heated 1.5 hrs. on a steam bath, then 1 hr. at 139°, the cooled mixture extracted with ligroine, and the product crystallized gave 0.2 g. ferrocenylacetothiomorpholide (XII), m. 127-8° (ligroine). Reduction of the reaction time of temperature afforded mixtures containing much unchanged ketone. XII (0.1 g.) refluxed 3 hrs. with 1 g. KOH in 2 ml. H<sub>2</sub>O and 8 ml. alcohol gave 55 g. V. β-Ferrocenylacrylic acid (0.1 g.) reduced

during 5 min. with 0.03 g. 10 percent Pd-C and H gave 0.1 g. VI. m. 117-18° (cyclohexane).  $\text{CH}_2(\text{CO}_2\text{Et})_2$  (5.5 g.) added to 0.3 g. Na in 50 ml. alcohol, then 5 g. III added, and the mixture refluxed 5 hrs. under N gave crude di-Et (ferrocenylmethyl) malonate, directly hydrolyzed with 10N NaOH to 0.7 g. (ferrocenylmethyl) malonic acid (XIII), m. 144-5°. Sublimation of XIII at 155°/0.3 and crystallization at -78° gave VI. Similar results were obtained when the reaction between the Na malonate derivative and the III was carried out 8 hrs. at 160°  $\text{Bu}_2\text{O}$ . III (5.01 g.) added to a solution of di-Et sodioformamidomalonate in alcohol, the mixture refluxed 19 hrs., filtered, the solvent removed,  $\text{H}_2\text{O}$  added, the mixture extracted with  $\text{Et}_2\text{O}$ , and evaporated gave 3.81 g. IV, m. 90-1° (aqueous alcohol). IV (1 g.) refluxed 1.5 hrs. with 1 g. NaOH in 7 ml.  $\text{H}_2\text{O}$  and 9 ml. alcohol acidified, filtered, the solid washed and recrystallized gave 0.43 g. (ferrocenylmethyl) formamidomalononic acid (XIV), m. 160-1° ( $\text{Me}_2\text{CO}$ -ligroine). IV (0.44 g.) refluxed 45 min. with 12 ml. 6N HCl, and evaporated, yielded 0.26 g. crude HCl salt, which, titrated in  $\text{H}_2\text{O}$  to pH 7, gave I, m. 200° (decomposition). I was obtained in lower over-all yield by the 2-step hydrolysis of IV to XIV followed by refluxing XIV 2 hrs. with 2N HCl. No hydrolysis occurred when IX was dissolved in 0.1N LiOH, brought to pH 8.1 with 0.1N phosphate buffer, and incubated 72 hrs. with carboxypeptidase. When refluxed 8 hrs. with 50 percent NaOH, 60 percent IX was covered and only a trace of unidentified ninhydrin-pos. product was formed. Complete destruction of all but 5 percent IX occurred on heating 6 hrs. with  $\text{H}_2\text{O}$  at 140-60°. Refluxing with 2N HCl had no effect, but 0.3 g. of this acid heated 17 hrs. in a sealed tube with 10 ml. GV HCl and 10 ml. BuOH gave 4 mg. I.

320. Nesmeyanov, A. N., Perevalova, E. G., Golovnya, R. V., Simukova, N. A., and Starovskii, O. V.,  
 REACTIVITY OF MONO- AND BIS (p-NITROPHENYL)  
 FERROCENE AND DIACETYLFERROCENE, Bulletin Academy  
 of Sciences of the USSR, Division of Chemical Sciences,  
 pp. 647-649, Izvestiya Akademii Nauk SSSR, Otdeleniye  
 Khimicheskikh Nauk, 1957, pp. 638-640.

Treatment of p-nitrophenylferrocene with  $\text{Hg}(\text{OAc})_2$  (sic) gave 15 percent bis (chloromercuri)-p-nitrophenylferrocene, red solid, soluble only in  $\text{Me}_2\text{CO}$ ; it decomposed on

heating. Adding 0.1 mole ferrocene in 200 ml. AcOH to  $p\text{-O}_2\text{NC}_6\text{H}_4\text{N}_2\text{Cl}$  (I) from 0.4 mole amine, stirring 2 hrs., and filtering gave 67 percent 1, 1'-bis (p-nitrophenyl) ferrocene, reduced with  $\text{SnHCl}$  to 81 percent bis (p-amino-phenyl) ferrocene, yellow, decomposition (from EtOH); its dibenzylidene derivative, m.  $222-3^\circ$  [from  $(\text{CH}_2\text{Cl})_2$ ]. Similarly, ferrocene gave 17 percent bis (p-bromophenyl) ferrocene, m.  $197-7.5^\circ$  (from petr. ether-EtOH). Adding I to diacetylferrocene in AcOH and stirring 0.5 hr. gave a precipitate which on leaching with  $\text{C}_6\text{H}_6$  and evaporating the solvent yielded 49 percent (p-nitrophenylazo) acetocyclopentadiene, red solid, decompose  $202-3^\circ$  (from  $\text{CHCl}_3$ ); no starting material was recovered. Similar reaction with  $\text{PhN}_2\text{Cl}$  gave 52 percent initial diacetylferrocene and 40 percent orange-red (phenylazo) acetocyclopentadiene, m.  $70-2^\circ$  (from aqueous EtOH), showing monomer molecular weight. Diacetylferrocene with  $p\text{-MeC}_6\text{H}_4\text{N}_2\text{Cl}$  was sluggish and after 1 hr. at  $40-50^\circ$  gave 72 percent starting material and 17 percent (p-tolueneazo) acetocyclopentadiene, m.  $105-7^\circ$  (from cyclopentane).

321. Rausch, M. D.,  
FERROCENYL ARYL ETHERS, U. S. Patent 3,064,026  
(Cl. 260-439), 13 November 1962, Applied 5 July 1960,  
4 pp. (CA 58, 10241a).

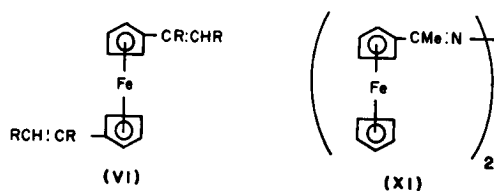
Not abstracted.

322. Riemschneider, R. and Helm, D.,  
STEREOISOMERIC FERROCENE-SUBSTITUTION PRODUCTS,  
Ann. Vol. 646, 1962, pp. 10-17.

Starting from ferrocene (I) a series of derivatives were prepared, and light absorption curves in benzene measured. A solution of 12 g. I and 25 g.  $p\text{-ClC}_6\text{H}_4\text{COCl}$  in 80 ml.  $\text{CS}_2$  was added to 30 g.  $\text{AlCl}_3$  in 50 ml.  $\text{CS}_2$ , refluxed 1 hr., poured onto ice, and precipitated product was recrystallized from benzene to give 15.5 g. 1, 1'-bis (p-chlorobenzoyl) ferrocene (II), m.  $186^\circ$ . I (18.5 g.) and 31 g.  $\text{BzCl}$  in  $\text{CS}_2$  in the presence of 40 g.  $\text{AlCl}_3$  gave 20.5 g. 1, 1'-dibenzoyl-ferrocene (III), m.  $104-6^\circ$ . To  $\text{PhCH}_2\text{MgCl}$  (from 2.4 g. Mg and 12.6 g.  $\text{PhCH}_2\text{Cl}$  in 80 ml. ether) was added 13 g. III in 200 ml. benzene, boiled 10 min., decomposed with 500 ml.



ice-5 percent HCl to give 8 g. 1, 1'-bis (1-hydroxy-1, 2-diphenylethyl) ferrocene (IV), m. 163-4° (MeOH).  $p\text{-ClC}_6\text{H}_4\text{-CH}_2\text{MgCl}$  (from 1.6 g. Mg and 12 g.  $p\text{-ClC}_6\text{H}_4\text{CH}_2\text{Cl}$  in 90 ml. ether) was treated with 12 g. II in 250 ml. benzene, boiled 0.5 hr., poured onto 300 ml. chilled 5 percent HCl to give 1, 1'-bis [1-hydroxy-1, 2-bis (p-chlorophenyl) ethyl] ferrocene (V), m. 212-15° (decomposition). V (5 g.) was heated with granular  $\text{KHSO}_4$  at 220-30° for 45 min. under N. After cooling the product was suspended in 20 ml.  $\text{PrOH}$ . The residue and precipitate from the filtrate were recrystallized from  $\text{PrOH}$  to yield 2.2 g. orange-brown VI ( $\text{R} = \text{Ph}$ ) (VII), m. 148-50°. V (8 g.) in 10 ml. Decalin was heated with  $\text{KHSO}_4$  at 220° under N. The dark reaction solution was warmed with 30 ml. petroleum ether and decanted. After renewed dilution with 30 ml. petroleum ether, red needles of VI ( $\text{R} = p\text{-ClC}_6\text{H}_4$ ) (VIII), m. 169-70° ( $\text{PrOH}$ ), were obtained. Further VIII was obtained from the petroleum ether layer, m. 161-2°. VII (1.0 g.) was dissolved in 230 ml. warm MeOH, hydrogenated with 0.3 g. Pd-C (90 ml. H) for 4.5 hrs., concentrated to 70 ml. and kept in an ice box to obtain 85 percent 1, 1'-bis (1, 2-diphenylethyl) ferrocene (IX), m. 106-7° (MeOH). Similar hydrogenation of VIII afforded IX. I (37 g.) and 120 ml.  $\text{Ac}_2\text{O}$  were treated with 8 ml. 85 percent  $\text{H}_3\text{PO}_4$  and 32 g. (70 percent) acetylferrocene (X) was obtained, m. 84-5° (EtOH). 1, 1'-Diacetylferrocene (1.7 g.) was prepared from 2 g. X and 1 ml.  $\text{AcCl}$  in 40 ml.  $\text{CS}_2$  in the presence of  $\text{AlCl}_3$ , m. 129-31° (MeOH). X (10 g.) in 50 ml. EtOH was treated with 2 g. 80 percent  $\text{NH}_2\text{NH}_2$ , boiled 5 hrs., and concentrated to obtain 1.8 g. XI, m. 218-20° (decomposition).



323. Schlogel, K. and Egger, H.,  
SYNTHESIS AND REACTIONS OF FERROCENYOYLACETALDE-  
HYDE AND FERROCENYL  $\beta$ -CHLOROVINYL KETONE,  
*Montash.*, Vol. 94, No. 6, 1963, pp. 1054-1063 (In German)  
(CA 59,7557f).

Successive additions of 4 g. Et formate and (with stirring) 9.2 g. acetylferrocene to 40 ml.  $C_6H_6$  containing 1 g. dispersed Na gave a precipitate of the enolate of ferrocenoylactaldehyde (I), which can be isolated in 77 percent yield. Hydrolysis with dilute  $H_2SO_4$ , ether extension treatment with  $NaHCO_3$  and flash evaporation gave 91 percent I, m.  $89-92^\circ$  (ligroine). Addition of 1.4 ml.  $PCl_3$  to 3.64 g. I in 80 ml.  $CCl_4$  under N at  $60^\circ$  in 30 min. gave a mixture that was poured into  $H_2O$  and extracted with  $CH_2Cl_2$ ; from this solution 46 percent ferrocenyl  $\beta$ -chlorovinyl ketone (II) was isolated, m.  $92-3^\circ$  (ligroine). The di-Me acetal (III) of I was obtained in 75 percent yield from 2 g. I in 40 ml. MeOH after the addition of 50 mg. p-toluenesulfonyl chloride, 1 hr. of heating to  $100^\circ$  and evaporation of the solvent, m.  $57-8^\circ$  (ligroine). The di-Et acetal was similarly obtained, m.  $51-4^\circ$ . III could also be obtained by heating a solution of II in MeOH with KOH. Addition of 0.45 g. III in 10 ml. tetrahydrofuran to a solution of 0.4 g.  $PhCH_2Cl$  and 0.1 g. Mg, followed by treatment with aqueous  $NH_4Cl$ , extraction with ether, and treatment with polyphosphoric acid gave 2 percent  $\beta$ -ferrocenyl naphthalene, isolated by thin layer chromatography, m.  $137-42^\circ$ . This compound as well as the  $\alpha$ -isomer, m.  $93-5^\circ$ , had earlier been obtained in the reaction of ferrocene and the naphthyl diazonium salts. Treatment of 0.2 g. II and 0.5 g.  $PhNH_2$  1 hr. at  $100^\circ$ , followed by the addition of ether and washing with 2N HCl and aqueous  $NaHCO_3$  gave 60 percent N-( $\beta$ -ferrocenoylvinyl) aniline, m.  $138-40^\circ$ . Saturation with HCl of a solution of 0.2 g. II, 0.2 g.  $AlCl_3$ , and 0.2 ml. mesitylene in 10 ml.  $CH_2Cl_2$  yielded (after 12 hrs.) 43 percent ferrocenyl mesitylvinyl ketone, m.  $151-3^\circ$ . This ketone could be similarly prepared in 15 percent yield from 2, 4, 6-trimethylcinnamoyl chloride and ferrocene; hydrogenation in AcOH with a Pd catalyst gave ferrocenyl 2-mesitylethyl ketone, m.  $113^\circ$ . A solution of 0.2 g. II in 10 ml. absolute ether was added to a solution of 2 g.  $NaNH_2$  in liquid  $NH_3$  to give 50 percent of the known ferrocenyl ethynyl ketone, m.  $77-80^\circ$ . Treatment of either I or II with

$\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$  at  $100^\circ$  30 min. gave the known 3-ferrocenylpyrazole, m.  $148-50^\circ$ . A mixture of 0.1 g. I, 5 ml. EtOH, 0.3 g. urea, and 0.3 ml. concentrated HCl, after 18 hrs. at room temperature, dilution with  $\text{H}_2\text{O}$ , and addition of KOH, was extracted with ether; the extract yielded 4-ferrocenyl-2-pyrimidone, m.  $212-13^\circ$  (decomposed). A solution of the Na enolate of I in HOAc slowly forms a precipitate of 1, 3, 5-triferrocenoylbenzene (57 percent in 18 hrs.), m.  $250^\circ$  (decomposition). Reduction of this compound 30 min. with  $\text{LiAlH}_4\text{-AlCl}_3$  in refluxing tetrahydrofuran gave 65 percent 1, 3, 5-triferrocenylbenzene. A di-Na enolate was obtained from 1, 1'-diacetylferrocene and Et formate in quantitative yield, as above. The corresponding oxoaldehyde, when treated with  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ , gave 16 percent 1, 1'-bispyrazolylferrocene, m.  $230^\circ$  (decomposed).

324. Schlogel, K. and Fried, M.,  
OPTICALLY ACTIVE HYDROCARBONS OF THE FERROCENE  
SERIES, Tetrahedron Letters, No. 22, 1963, pp. 1473-1478  
(In German).

See item No. 14 for abstract.

325. Sokolova, E. B., Shebanova, M. P., and Chou, H.,  
SYNTHESIS OF FERROCENE ANALOGS, Zhurnal Obshchei  
Khimii, Vol. 33, 1963, pp. 217-220.

Refluxing alkylindenes with 1.5 moles BuLi in  $\text{Et}_2\text{O}$  2 hrs. gave 80-95 percent  $\text{C}_4\text{H}_{10}$ , while the solution of the Li derivatives was treated with 0.6 mole  $\text{FeCl}_2$  1 hr. at room temperature and 2 hrs. at reflux and after treatment with aqueous HCl, gave the following ferrocene analogs after removal of starting material with superheated steam and sublimation of the residue in vacuo: bis (ethylindenyl) iron, violet-black; bis (allylindenyl) iron, violet-black; bis (butylindenyl) iron, 20 percent violet-black; bis (phenylindenyl) iron, 18 percent black; bis (benzylindenyl) iron, 10 percent, black, m.  $131-3^\circ$ . All were stable in dry air, but decomposed in hydrocarbons or ethers, yielding unidentified brown products. The following constants of starting materials were determined: 3-ethylindene,  $b_{745}$   $224^\circ$ ,  $d_{20}$  0.9744,  $n_D^{20}$  1.5601; 3-butylin-dene,  $b_{17}$   $129.5-30^\circ$ , 0.9479, 1.5410; 3-allylindene,  $b_5$   $191-2^\circ$ , 0.9990, 1.5760; 3-phenylindene,  $b_{28}$   $201^\circ$ , 1.0826, 1.6345; 3-benzylindene, m.  $33^\circ$ ,  $b_7$   $166-7^\circ$ .

326. Wyandotte Chemicals Corporation, Michigan,  
INTERMEDIATES FOR HIGH-TEMPERATURE STABLE  
POLYMERS. REPORT FOR 1 FEBRUARY 1963 - 31  
DECEMBER 1963 by P. Szecsi, J. D. Behun, P. T. Kan,  
and R. A. Moore, January 1964, Report No. ML TDR64 9,  
AD-439 847, Contract No. AF33 657 10819 (Unclassified Report).

Synthetic methods and experimental procedures employed in the preparation of specified intermediates for high-temperature stable polymers are described.

In some cases, known procedures were modified in order to facilitate large-scale laboratory preparations. In a few instances, where procedures were not available, some exploratory effort was expended to develop preparative methods. The following compounds were synthesized in a high state of purity by published and/or adapted procedures:

- 1) 2,4-Diphenyl-6-chloro-s-triazine
- 2) 2,4-Dibromo-6-phenyl-s-triazine; diferrocenylketone; diferrocenylmercury
- 3) 1,1'-Diiodoferrocene
- 4) Ferrocene monoboronic acid
- 5) Poly-m-phenoxylenes
- 6) Dichlorodiphenylgermanium
- 7) 2-Hydroxyisophthalic acid. Trifluoropyrimidine and triphenylaluminum were procured directly.

### Section III. REACTIONS OF FERROCENE DERIVATIVES

#### A. Ferrocene, Bridged Ferrocenes, and Alkyl Ferrocenes

327. Beckwith, A. L. J. and Leydon, R. J.,  
MECHANISM OF THE REACTION OF FERROCENE WITH FREE  
RADICAL REAGENTS, Tetrahedron Letters, 1963, pp. 385-  
388 (cf. CA 51,324 h).

Ferrocene (FcH) in  $C_6H_6$  treated with  $Bz_2O_2$  or  $PhCO_2OCMe_3$  gave high yields of  $Fe(BzO)_3$ . The intermediate formation of ferricinium ion ( $FcH^+$ ) in these reaction was demonstrated by continuous extraction of the mixture with dilute  $H_2SO_4$  to yield 78 percent  $FcH^+$  with a corresponding decrease of the yield of  $Fe(BzO)_3$ . Treatment of FcH with  $PhN(NO)Ac$  in  $C_6H_6$  gave phenylferrocene and diphenylferrocene but extraction of the mixture with dilute  $H_2SO_4$  yielded  $FcH^+$  only. The unreactivity of FcH to attack by free radicals under conditions precluding concomitant formation of  $FcH^+$  was demonstrated by its recovery after treatment with  $NCMe_2CN$ :  $NCMe_2CN$ , with  $tert-Bu_2O_2$  in  $PhMe$ , or  $(PhN_2)_3ZnCl_4$  and Zn powder in  $Me_2CO-C_6H_6$ , in agreement with the unreactivity of FcH with Ph free radicals generated from  $PhN:NCPh_3$  or  $PhMgBr$ . In contrast  $(FeH^+)_2SO_4$  treated with  $NCMe_2CN$ :  $NCMe_2CN$  in aqueous alcohol yielded 2-cyano-2-ferrocenylpropane,  $C_{14}H_{15}FeN$ , m.  $63-4^\circ$ , also synthesized by a conventional route. Since  $NCCMe_2^\circ$  is a relatively stable radical incapable of attacking lower aromatic hydrocarbons, the high reactivity of  $FcH^+$  towards free radicals is demonstrated. FcH and anthracene treated with  $(PhN_2)_2SO_4$  in  $C_6H_6-AcOH$  with rapid evolution of N gave 9-phenylanthracene and  $Ph_2$ , both indicative of Ph free radical formation. The same products were obtained when FcH and anthracene were heated with  $PhN(NO)Ac$  in  $C_6H_6$ . It was supposed that reaction of FcH with  $Bz_2O_2$ ,  $PhN(NO)Ac$ , and  $PhN_2^+$  involve intermediate formation of FcH. A one-electron transfer between FcH and  $PhCO_3^\circ$  radical was also postulated. The moderate yield of  $FcCH_2Ph$ , m.  $74-5^\circ$ , from treatment of FcH with  $PhCO_3Bu-tert$  in  $PhMe$  was accordingly anticipated.

328. Benkeser, R. A. and Bach, J. L.,  
FACTORS GOVERNING ORIENTATION IN METALATION  
REACTIONS. III. METALATION OF ALKYLFERROCENES,  
American Chemical Society Journal, Vol. 86, No. 5, 1964,  
pp. 890-895 (cf. CA 60, 4029 f).

A systematic study of the metalation of methyl-, ethyl-, isopropyl-, and tert-butylferrocene by AmNa and AmK has been made. The monometalation products in these reactions consisted of a mixture of 3- and 1'-metalloalkylferrocenes in an approximate ratio of 1:2.6. A statistical distribution would be 1:2.5. Despite a 1:1 molar ratio of alkylferrocene to metalating agent, dimetalation was predominant in these reactions. It was established by nuclear magnetic resonance spectroscopy, that the major dimetalation product in each case was the 3, 1'-dimetalloalkylferrocene. The dianion is thermodynamically more stable than the monoanion, which accounts for its preferential formation. Even in metalations of ferrocene and alkylferrocenes with BuLi (1:1 molar ratio), which were carried out in a homogeneous fashion, there was produced about a 3:2 mixture of mono- to dimetalation products. There was no observable tendency for the metal atom in any of these metalations to revert from the ring to the side chain in contradistinction to results with alkylbenzenes. Apparently the ring carbanions are more stable than the corresponding  $\alpha$ -carbanions in the ferrocene system.

329. Brandeis University, Waltham, Massachusetts,  
MECHANISM OF ELECTROPHILIC SUBSTITUTION OF  
FERROCENES by M. Rosenblum, October 1962, Report  
No. AROD 3064 4, AD-289 022 (Unclassified Report).

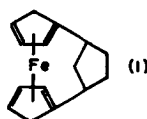
Two mechanisms by which metallocenes undergo electrophilic substitution will be considered. The first, exocyclic attack of the electrophilic reagent upon the formally unsaturated rings, is in principle a mechanism analogous to that pertaining to benzenoid systems. The second mechanism invokes the metal atom itself as the initial site of electrophilic attack. Subsequent rearrangement of this intermediate, involving encocyclic attack, leads eventually to the substituted ferrocene. Attempts were made to distinguish between these two courses of reaction by conducting acylation reactions on a series of bridged ferrocenes which offered varying degrees of steric occlusion at the metal atom. Vapor phase analysis of the acyl isomers formed in the course of  $\text{AlCl}_3$  catalyzed I-butyrylation of ferrocene gave the data for the ratio of 3 to 2 substitution.

30. Bublitz, D. E.,  
RING MIGRATION IN ALKYLATED FERROCENES, Canadian Journal of Chemistry, Vol. 42, No. 11, 1964, pp. 2381-2384.

Alkylferrocenes have been found to undergo disproportionation to ferrocene and 1,1'-dialkylferrocenes in the presence of  $\text{AlCl}_3$  or  $\text{GaCl}_3$ . The mechanistic pathway has been shown to involve ( $\pi$ -ligand) ( $\pi$ -ligand) exchange as opposed to the usual C-C cleavage found in benzene chemistry.

331. Cottis, S. G. and Rosenberg, H.,  
CLEAVAGE OF FERROCENE BY ALUMINIUM CHLORIDE:  
CYCLOPENTYLFERROCENES, Chemistry and Industry, 1963,  
pp. 860-861.

Ferrocene was cleaved in benzene solution by refluxing in the presence of  $\text{AlCl}_3$  to yield 1,1'-(1,3-cyclopentyl) ferrocene (I), m.  $140^\circ$ . The structure of I was assigned by comparison of its infrared and nuclear magnetic resonance spectra to those of phenylcyclopentylferrocene.



332. Group, E. F., Jr.,  
A STUDY OF CERTAIN METALATION AND CONDENSATION  
REACTIONS OF FERROCENE AND MONOSUBSTITUTED  
FERROCENES, University Microfilms (Ann Arbor, Michigan),  
Order No. 63-287, 95 pp, Dissertation Abstract, Vol. 23, 1963,  
pp. 2693-2694.

The preparations of some new derivatives of ferrocene are described.

Ferrocene was converted to ferrocenecarboxaldehyde by the formylation reaction employing phosphorus oxychloride and N-methylformanilide. The aldehyde was reacted with bromogorm and potassium hydroxide in methanol to give  $\alpha$ -methoxyferroceneacetic acid. The intermediate in the previous reaction, ferrocenyltrichloromethylcarbinol, was prepared by the base-catalyzed condensation of ferrocenecarboxaldehyde with chloroform, and the isolated product was converted to  $\alpha$ -methoxyferroceneacetic acid by the action of potassium hydroxide in methanol.

Several attempts to prepare  $\alpha$ -aminoferroceneacetic acid from the reaction of ferrocenyltrichloromethylcarbinol with potassium amide in liquid ammonia were unsuccessful.

Ferrocenyltrichloromethylcarbinol was also prepared by the reaction of ferrocene and chloral with aluminum chloride. Three different derivatives of ferrocene were isolated from the reaction product: ferrocenyltrichloromethylcarbinol, an olefin identified as 1,1-dichloro-2-ferrocenylethylene, and the symmetrically disubstituted trichloromethylcarbinol of ferrocene.

The mercuration of ferrocene was carried out using mercuric acetate; treatment of the reaction mixture with lithium chloride gave a separable mixture of chloromercuriferrocene and 1,1'-dichloromercuriferrocene. The chloromercuriferrocene was converted to lithioferrocene by reaction with *n*-butyllithium.

Several unsuccessful attempts were made to prepare ferrocenyltrichloromethylcarbinol by reacting lithioferrocene with chloral. The reaction of 3,3,3-trichloro-1,2-epoxypropane with lithioferrocene also failed to give the desired trichloromethylcarbinol derivative.

Lithioferrocene was shown to react normally with epoxides containing no trichloromethyl group; alcohol derivatives of ferrocene were prepared in this manner from ethylene oxide, propylene oxide and styrene oxide.

Ferrocenyltrichloromethylcarbinol was successfully prepared from chloromercuriferrocene and chloral with aluminum chloride, but the same reaction failed to give the disubstituted trichloromethylcarbinol when applied to 1,1'-dichloromercuriferrocene.

The Grignard reagent of ferrocene was prepared from lithioferrocene, and carbonation gave ferrocenecarboxylic acid. The Grignard reagent was reacted successfully with chloral to give ferrocenyltrichloromethylcarbinol, but failed to give the desired trichloromethylcarbinol when reacted with 3,3,3-trichloro-1,2-epoxypropane. Attempts to secure the di-Grignard reagent of ferrocene from 1,1'-dichloromercuriferrocene were unsuccessful.

Nickelocene was prepared by reaction of anhydrous nickel bromide with cyclopentadiene in diethylamine. Neither the formylation nor the mercuration reaction could be successfully applied to nickelocene.



333. Kansas University, Lawrence, Kansas,  
ELECTROCHEMISTRY OF ORGANIC COMPOUNDS IN NON-  
AQUEOUS MEDIA by W. E. McEwen and J. Kleinberg,  
September 1962, Report No. AROD 2498 3, AD-285 695  
(Unclassified Report).

Unusual reactions of anhydrous  $\text{AlCl}_3$  with ferrocene in  $\text{CCl}_4$  at room temperature.

334. Nesmeyanov, A. N., Kochetkova, N. S., and Materikova, R. B.,  
DESTRUCTION OF CYCLOPENTADIENYL COMPOUNDS OF  
METALS BY BROMINE AND POTASSIUM HYPOBROMITE,  
Doklady Akademii Nauk SSSR, Vol. 147, 1962, pp. 113-116.

$(\text{C}_5\text{H}_6)_2\text{Hg}$  and Br in heptane- $\text{C}_6\text{H}_6$  at  $-20^\circ$  instantly gave  $\text{HgBr}_2$  and 93 percent tribromocyclopentane, m.  $63-4^\circ$ ; reaction run at  $2-5^\circ$  gave isomeric pentabromocyclopentanes, m.  $96-101^\circ$  and  $105-7^\circ$  in 49 percent total yield. Similarly  $\text{C}_5\text{H}_5\text{Tl}$  at  $-20^\circ$  gave 35 percent tribromocyclopentane, m.  $62.5-4^\circ$ ; reaction at  $20^\circ$  gave 51 percent pentabromocyclopentane, m.  $103-4^\circ$ . Ferrocene and Br similarly gave 43 percent tribromocyclopentane. Pentaethanoferrocene and Br at  $-20^\circ$  similarly gave 61 percent tribromocyclopentane, m.  $60-2^\circ$ , along with a substance  $\text{C}_{20}\text{H}_{21}\text{Br}_7$ , m.  $65-70^\circ$ , which readily lost HBr unless kept below  $-20^\circ$ .  $(\text{C}_5\text{H}_5)_2\text{Hg}$  and KOBr solution in  $\text{H}_2\text{O}-\text{C}_6\text{H}_6$  gave in 2 hrs. at  $2^\circ$  61 percent  $\text{C}_5\text{Br}_6$ , m.  $86-6.5^\circ$ .  $\text{C}_5\text{H}_5\text{Tl}$  and KOBr also gave 55 percent  $\text{C}_5\text{Br}_6$ . Ferrocene and KOBr gave a precipitate containing Fe(III) and a mixture of  $\text{C}_5\text{Hr}_5$ , m.  $100-2^\circ$ , which were separated by chromatography on  $\text{SiO}_2$  in heptane; some 60 percent ferrocene was recovered. Ferrocene and KOI solution showed no evidence of reaction. A small amount of  $\text{C}_5\text{HBr}_5$  was detected among the reaction products of  $\text{C}_5\text{H}_5\text{Tl}$ .

335. Nesmeyanov, A. N., Perevalova, E. G., Yur'eva, L. P., and Kakurina, L. N.,  
REACTION PRODUCTS OF CYANATION OF METHYL- AND ETHYLFERROCENES, Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 10, 1964, pp. 1897-1899 (In Russian).

Refer to item No. 247 for abstract.

336. Nesmeyanov, A. N., Vol'kenau, N. A., and Bolesovia, I. N.,  
LIGAND EXCHANGE IN FERROCENE, Doklady Akademiya  
Nauk SSSR, Vol. 149, No. 3, 1963, pp. 615-618.

Refluxing ferrocene with  $\text{AlCl}_3$  and Al dust in  $\text{C}_6\text{H}_6$  6 hrs. under N gave after an aqueous treatment a yellow aqueous solution of benzenecyclopentadienyliron (I), which was precipitated as the tetraphenylborate salt,  $\text{C}_{35}\text{H}_{31}\text{BFe}$ , yellow decomposed  $250-1^\circ$ , in 60 percent conversion. Similar reaction in mesitylene gave 66 percent mesitylencyclopentadienyliron tetraphenylborate (II), decomposed  $257-8^\circ$ . In tetrahydronaphthalene as solvent, the reaction gave in 3.5 hrs. 48 percent tetrahydronaphthalenecyclopentadienyliron tetraphenylborate, decomposed  $237.5-8.5^\circ$ . Heating diacetylferrocene with  $\text{AlCl}_3$  in mesitylene 4.5 hrs. gave after addition of  $\text{Ph}_4\text{BNa}$  22 percent mesityleneacetylcyclopentadienyliron tetraphenylborate, decomposed  $199-200^\circ$ , along with a tetraphenylborate salt of an unidentified cation, decomposed  $214-15^\circ$ . II and aqueous  $\text{KMnO}_4$  at  $95^\circ$  gave in 11 hrs. trimesic acid. I in aqueous solution treated with KI-iodine gave  $\text{C}_{11}\text{H}_{11}\text{FeI}_3$ , lilac-red, decomposed  $226-7^\circ$ ; excess KI-iodine gave a dark polyiodide with indefinite decomposition temperature, which with  $\text{Na}_2\text{SO}_3$  gave benzenecyclopentadienyliron iodide, yellow, decomposed  $230-30.5^\circ$ , which was sensitive to light, O, and peroxides; iodine gave the triiodide shown above. Heating the iodide in vacuo to  $240^\circ$  gave ferrocene and a residue containing Fe. Other mixed complexes shown above decomposed to ferrocene at about  $300^\circ$ , also yielding ferrocene after initial formation of  $\text{Ph}_2$ .

337. Nesmeyanov, A. N., Vol'kenau, N. A., Woodward, et al.,  
ACYLATION OF ACETYL- AND ETHYLFERROCENES,  
Doklady Akademiya Nauk SSSR, Vol. 111, 1956, pp. 605-608  
(cf. CA 50, 15519h and CA 48, 20539).

Refer to item No. 183 for abstract.

338. Neuse, E. W. and Trifan, D. S.,  
ALKYLATION OF FERROCENE WITH  $\alpha$ -ARYL ALCOHOLS,  
American Chemical Society Journal, Vol. 84, 1962, pp. 1850-1856.

A mixture of 4.29 g ferrocene (I), 2 g.  $\text{Ph}_3\text{COH}$  (II) and 0.1 g. anhyd.  $\text{AlCl}_3$  was heated 1 hr. under N at  $140^\circ$ . The mixture was extracted with MeOH and the residue dissolved in cyclohexane and chromatographed on  $\text{Al}_2\text{O}_3$  (2.5 X 70 cm. column). Development with 1:1 cyclohexane-petr. ether and then with petr. ether, and extraction of the orange yellow layer with  $\text{C}_6\text{H}_6$  gave 2.55 g. triphenylmethylferrocene (III), m.  $190^\circ$  ( $\text{C}_6\text{H}_6$ ). When the above reaction was carried out using molar ratio I-II = 1:1.5, 1, 1'-ditritylferrocene (IV) was obtained in 95 percent yield, as orange needles, m.  $286^\circ$ . With the molar ratio I-II = 1 the yields were 50 percent III, 36 percent IV. A mixture of 2 g. I, 5.98  $\text{Ph}_3\text{CCl}$  (V), and 0.2 g.  $\text{AlCl}_3$  was heated at  $130^\circ$  1 hr. to give 2.9 g. IV. IV was also obtained in 42 percent yield using the molar ratio I-V- $\text{AlCl}_3$  = 2:1:2. A by-product  $\text{C}_{105}\text{H}_{80}\text{Fe}$  not melting up to  $300^\circ$  was also obtained. The reaction of I with benzhydrol (VI) using the molar ratio I-VI 2 and 10 percent  $\text{AlCl}_3$  (based on weight of VI) gave after chromatography 45 percent 1, 1'-dibenzhydrylferrocene (VII), m.  $164.5-5^\circ$ . With VI-I ratio of 2.2, and 9 percent  $\text{AlCl}_3$ , 55 percent of VII was obtained after chromatography besides another compound.  $\text{C}_{62}\text{H}_{50}\text{Fe}$ , m.  $80-130^\circ$ . Under Friedel-Crafts conditions using a molar ratio of VI-I- $\text{AlCl}_3$  3:1:2.5, 10 percent VII could be obtained besides large quantities of polysubstituted materials. Using VI-I- $\text{SnCl}_4$  = 2.2:1:-2.2 in dioxane, VII could be obtained in 43 percent. A well-powdered mixture of 2.2 g. I, and 0.4 g.  $\text{AlCl}_3$  was heated at  $130-40^\circ$  with 2-phenylpropan-2-ol (VIII) and the product separated by chromatography and crystn. into 1 g. 1, 1'-bis(2-phenylpropyl)ferrocene (IX), m.  $136-7^\circ$  (hexane) and a compound,  $\text{C}_{28}\text{H}_{30}\text{Fe}$  (X) m.  $179-80^\circ$  (EtOH). In a modified procedure, 2.2 g. I and 1.1 g.  $\text{ZnCl}_2$  was heated with 3.22 g. (VIII) at  $110-15^\circ$  for 1 hr. and 0.12 g.  $\text{AlCl}_3$  was added and the mixture heated at  $120-5^\circ$  1.5 hrs. Extraction with  $\text{C}_6\text{H}_6$  gave 3 g. IX. A mixture of 2.5 g. I, 0.55 g.  $\text{AlCl}_3$  added in 3 lots, and 2.2 g. 1, 1-diphenylethylene was heated at  $160-5^\circ$ . Extraction with  $\text{C}_6\text{H}_6$  and fractional extraction with EtOH gave 0.67 g. 1, 1-diphenylferrocene (XI), m.  $131-2^\circ$  (hexane-EtOH), and 0.9 g. 1, 1'-bix(1, 1'-diphenylethyl)ferrocene (XII), m.  $210^\circ$  ( $\text{HCONMc}_2$ ). A mixture of 8.84 g. I, 3.52 g.  $\text{AlCl}_3$ , and 80 g. polyphosphoric acid was stirred at  $100^\circ$ , 3.52 g. tert-BuOH was dropped under

N, and the mixture heated at 120° for 4 hrs. Chromatography over Al<sub>2</sub>O<sub>3</sub> gave 2.5 g. tert-butylferrocene (XIII), b<sub>5</sub> 105-12°. Using gaseous BF<sub>3</sub> instead of AlCl<sub>3</sub> in the above reaction, gave two tributyl compounds. The mechanism of these reactions as well as a few infrared correlations are discussed.

339. O'Conner, G. N., Crawford, J. V., and Wang, C. H.,  
REDUCTION OF PYRROLYL-2, 3, 4, 5-TETRAMERCURIC  
ACETATE WITH FERROCENE, Journal of Organic Chemistry  
Vol. 30, No. 12, 1965, pp. 4090-4091.

Pyrrolyltetrameric acetate was prepared and characterized by elementary and infrared spectral analysis. The pyrrolylmercuric cation from solvolysis of the parent compound in acetic acid-toluene was reduced by ferrocene and the major product of the reaction was identified as pyrrole. The free-radical mechanism of the reaction was presented.

340. Plastics Laboratory,  
REDUCTIVE CLEAVAGE OF FERROCENE by D. S. Trifan  
L. Nicholas, Technical Report No. 42A, Report No. 3A,  
AD-102 012, Contract No. DA-36-0395C-70154 (Unclassified  
Report).

A mild reductive degradation, which effects cleavage of the ferrocene molecule into its iron and two 5-carbon ring constituents is accomplished using lithium in ethylamine. Other metal-anime ammonia combinations similarly reduce ferrocene. Cleavage proceeds by attack of lithium on carbon, displacing the ring electrons to the conjugated double bond orbitals with resulting detachment of the cyclopentadienyl carbanion from the iron atom.

Complete resistance of ferrocene to catalytic hydrogenation, even over rhodium on alumina for extended periods was demonstrated.

341. Purdue University, Lafayette, Indiana,  
CHEMISTRY OF FERROCENE AND RELATED COMPOUNDS,  
FINAL REPORT by R. A. Benkeser, January 1963, Report  
No. AFOSR, 4498, AD-600 969, Contract No. AF49 638 297  
(Unclassified Report)

Researches on the following areas of study are summarized:  
Electrical effects in ferrocene; addition reactions of vinyl-ferrocene; and alkylferrocene metalation.

42. Richards, J. H.,  
REACTIONS OF METALLOCENES, Official Digest of Paint  
Research Institute, Vol. 36, No. 479, 1964, p. 1433.

Metallocenes have been found to play important roles as catalysts in some photochemical processes. In particular, ferrocene catalyzes the cis-trans isomerization of various olefins such as piperylene and stilbene. Ferrocene also catalyzes the dimerization of piperylenes and internal cycloaddition of 1,5-cyclooctadiene. On the other hand, ferrocene quenches the phosphorescence of anthracene at a diffusion-controlled rate. Quantitative studies of these reactions have been made and a mechanism for the photo-chemical behavior of metallocenes has been developed and is presented.

343. Rinehart, K. L., Jr., Bublitz, D. E., and Gustafson, D. H.,  
ORGANIC CHEMISTRY OF FERROCENE. VI. ACETYLATION  
OF MONO-, DI-, AND TRI-BRIDGED FERROCENES, American  
Chemical Society Journal, Vol. 85, 1963, pp. 970-982 (cf.  
CA 57, 16650g).

Bis- and tris (trimethylene) ferrocenes were synthesized. These compounds and the mono-bridged analog were acetylated and the ratios of the isomeric Ac compounds determined. Cyclization of certain bridged ferrocenepropionic acids was shown to give homoannular ketonic products, as well as the expected heteroannular compounds.  $\text{Ac}_2\text{O}$  (0.90 g.) in 100 ml.  $\text{CH}_2\text{Cl}_2$  added dropwise to 2.00 g. 1,1'-trimethyleneferrocene (I) and 2.59 g.  $\text{AlCl}_3$  in 100 ml.  $\text{CH}_2\text{Cl}_2$  at reflux temperature under N, the whole refluxed 14-18 hrs., cooled, poured over ice, treated with ascorbic acid to reduce any ferricinium ions present, the aqueous layer separated, extracted repeatedly with  $\text{CH}_2\text{Cl}_2$ , and the combined organic solutions worked up to give 0.285 g. I, 0.748 g. 2-acetyl-1,1'-trimethyleneferrocene (II), m. 78.0-8.5° (hexane), 1.245 g. 3-acetyl-1,1'-trimethyleneferrocene (IIa), m. 99-100° (hexane), and 0.119 g. 3,4'-diacetyl-1,1'-trimethyleneferrocene (III), m. 131-2° (hexane). II (1.0 g.) in 150 ml. xylene added dropwise to 0.32 g. 50 percent NaH in mineral oil suspension and 0.78 g.  $(\text{EtO})_2\text{CO}$  (IV) in 225 ml. xylene at reflux temperature with stirring, under N, the whole refluxed 12 hrs., cooled to room temperature, hydrolyzed with ice  $\text{H}_2\text{O}$  containing 10 millimoles HCl, the organic layer separated, dried evaporated, the residual oily  $\beta$ -keto propionic acid ester compound dissolved in 40 ml. AcOH, the solution hydrogenated 46 hrs. over 1.0 g.  $\text{PtO}_2$

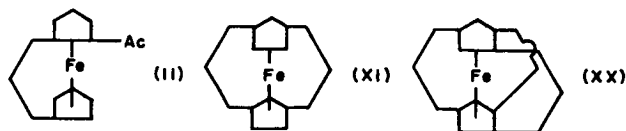
at 40 psi, filtered, the filtrate evaporated (rotary evaporator) the residual crude ester (1.1 g.) refluxed 2 hrs. in 50 ml. EtOH containing 4.0 ml. 2N NaOH, the solution diluted with H<sub>2</sub>O, washed repeatedly with Et<sub>2</sub>O, acidified with H<sub>3</sub>PO<sub>4</sub>, extracted with Et<sub>2</sub>O, the extract dried, evaporated, the residual crude propionic acid compound (0.9 g.) dissolved in 200 ml. CCl<sub>4</sub> (previously deoxygenated by bubbling with N) and 4.0 g. (CF<sub>3</sub>-CO)<sub>2</sub>O (V), the solution stirred 4 hours in the dark in a stoppered flask, poured into excess aqueous NaHCO<sub>3</sub>, the aqueous layer separated, extracted with CH<sub>2</sub>Cl<sub>2</sub>, the organic extracts dried, evaporated, and the residue chromatographed on Al<sub>2</sub>O<sub>3</sub> gave 0.206 g. 2,2'-( $\alpha$ -oxotrimethylene)-1,1'-trimethyleneferrocene (VI), decompose above 220° (Skellysolve B), and 0.053 g. 3,2'-( $\alpha$ -oxotrimethylene)-1,1'-trimethyleneferrocene, m. 132.0-3.0°. VI (0.53 g.) in 100 ml. Et<sub>2</sub>O added dropwise to 0.30 g. AlCl<sub>3</sub> and 0.087 g. LiAlH<sub>4</sub> in 100 ml. Et<sub>2</sub>O with stirring at reflux temperature, the whole refluxed 30 min., cooled in an ice bath, decomposed with wet Et<sub>2</sub>O, treated with H<sub>2</sub>O, the organic layer separated, dried, and evaporated gave 0.462 g. 1,1':2,2'-bis(trimethylene)-ferrocene (VII), m. 216-18° (hexane). Similar treatment of 10.0 g. IIa, 3.5 g. 50 percent NaH-mineral oil dispersion, and 8.8 g. IV in 75 ml. (total) C<sub>6</sub>H<sub>6</sub> gave 12.2 g. crude  $\beta$ -oxo propionic acid ester compound (VIII). Hydrogenation of VIII over 1.0 g. PtO<sub>2</sub> at 40 psi followed by sapon. gave 6.7 g. crude propionic acid compound (IX). Crude IX (6.7 g.) and 25 ml. V in 200 ml. CCl<sub>4</sub> treated as above gave 6.3 g. 3,3'-( $\alpha$ -oxotrimethylene)-1,1'-trimethyleneferrocene (X), m. 107-10°. X (0.73 g.) reduced with 0.99 g. LiAlH<sub>4</sub>-5.2 g. AlCl<sub>3</sub> as above gave quantitative 1,1':3,3'-bis(trimethylene) ferrocene (XI), m. 89.0-91.5° (hexane). 1,1'-Diacetylferrocene (prepared by method of Rosenblum and Woodward, CA 53, 10161f) (5.60 g.) in 250 ml. dry C<sub>6</sub>H<sub>6</sub> added dropwise during 1 hr. to 3.94 g. 50 percent NaH-mineral oil dispersion and 9.64 g. dry IV in 250 ml. C<sub>6</sub>H<sub>6</sub> with stirring, the whole stirred 5 hrs. at room temperature, refluxed 5 hrs., cooled, treated with absolute EtOH followed by ice and HCl, the organic phase separated, dried, concentrated, and the residual oil separated by decanting the IV present gave 5.9 g. crude bis ( $\beta$ -oxo) ester (XII). Crude XII in AcOH hydrogenated over PtO<sub>2</sub> at room temperature and 10-15 atm. (H absorption ceased after 24-48 hrs.), the solution filtered, the filtrate poured into H<sub>2</sub>O, partially neutralized with aqueous NaOH, extracted with Et<sub>2</sub>O, the extract washed with aqueous NaHCO<sub>3</sub> and H<sub>2</sub>O, dried, and

concentrated gave 5.5 g. crude corresponding hydrogenated ester (XIII). XIII refluxed with a slight excess N NaOH in EtOH-H<sub>2</sub>O, the solution cooled, and acidified with H<sub>3</sub>PO<sub>4</sub> gave 3.1 g. 1,1'-ferrocenedipropionic acid (XIV), m. 135-7°. In other runs, the yields of XII, XII, and XIV were 74 percent, 87 percent, and 75 percent, respectively XIV (4.8 g.), 250 ml. deoxygenated CCl<sub>4</sub>, and 24 g. V stirred 4 hrs. at room temperature under N in the dark, poured into excess aqueous NaHCO<sub>3</sub>, the aqueous layer separated, extracted with CH<sub>2</sub>Cl<sub>2</sub>, the combined organic solutions washed with H<sub>2</sub>O, dried and concentrated gave 4.5 g. crude keto-bridged propionic acid mixture. (XV). Crude XV (4.5 g.) hydrogenated 24 hrs. over 1.0 g. PtO<sub>2</sub> at room temperature and 40 psi the solution filtered, the filtrate poured into H<sub>2</sub>O, extracted with Et<sub>2</sub>O, the extract washed neutral with H<sub>2</sub>O, dried, and concentrated gave 3.9 g. crude mixture (XVI) of 1,1'-trimethyleneferrocene-2- and 3-propionic acids. Crude XVI cyclized as above and the neutral product from the cyclization chromatographed on Al<sub>2</sub>O<sub>3</sub>, gave 0.10 g. VI, decompose above 225° (Skellysolve B), and 0.99 g. X, m. 111.0-12.3°. AlCl<sub>3</sub> (0.40 g.) and 0.32 g. Ac<sub>2</sub>O in CH<sub>2</sub>Cl<sub>2</sub> added dropwise to 0.75 g. VII in 25 ml. refluxing CH<sub>2</sub>Cl<sub>2</sub> with stirring under N, the whole refluxed 8 hrs. and worked up gave 0.162 g. unchanged VII, 0.339 g. 3-Ac derivative (XVII) of VII, m. 162.0-3.5° (Skellysolve B), and 0.24 g. 4-Ac derivative (XVIII) of VII, m. 126.0-7.5° (hexane). XVII (0.52 g.) treated as above with 3.8 millimoles NaH and 0.48 g. IV in 60 ml. xylene, the whole refluxed 16 hrs., worked up as usual, the resulting β-keto ester hydrogenated over 0.5 g. PtO<sub>2</sub> at 40 psi, the isolated reduced ester refluxed in alcohol-NaOH, the resulting crude acid stirred 4 hrs. in the dark with 50 ml. CCl<sub>4</sub> and 2 ml. V, the solution worked up as usual, and the neutral product chromatographed on Al<sub>2</sub>O<sub>3</sub> gave 0.045 g. 3,3'-(α-oxotrimethylene)-1,1':2,2'-bis(trimethylene) ferrocene (XIX), m. 190-3° (Skellysolve B), and 0.102 g. 4,3-(α-oxotrimethylene)-1,1':2,2'-bis(trimethylene) ferrocene, m. 160-3° (hexane-C<sub>6</sub>H<sub>6</sub>). Reduction of 30 mg. XIX with a 10-fold excess LiAlH<sub>4</sub>-AlCl<sub>3</sub> gave 28.6 mg. 1,1':2,2':3,3'-tris(trimethylene) ferrocene, m. 178-81° (sublimation in vacuo). XVIII (0.356 g.) treated as above with 2.20 millimoles NaH and 0.28 g. IV in 40 ml. xylene, refluxed 18 hrs., the resulting β-keto ester hydrogenated over 0.5 g. PtO<sub>2</sub> at 40 psi, the reduced ester sapond., the crude propionic acid compound (0.50 g.) stirred 4 hrs. in the dark with 20 ml. CCl<sub>4</sub> and 2 ml. V, worked up as usual,

and the neutral product chromatographed on  $\text{Al}_2\text{O}_3$  gave 0.177 g. 4,4'-( $\alpha$ -oxotrimethylene)-1,1':2,2'-bis (trimethylene) ferrocene (XIXa), m. 170-2° (hexane). Reduction of 50 mg. XIXa with excess  $\text{LiAlH}_4$ - $\text{AlCl}_3$  as above gave quantitative 1,1':2,2':4,4'-tris (trimethylene)-ferrocene (XX), m. 145-51°.  $\text{AlCl}_3$  (1.75 g.), 1.32 g.  $\text{Ac}_2\text{O}$ , and 2.29 g. XI in 200 ml.  $\text{CH}_2\text{Cl}_2$  stirred 18 hrs. at room temperature, and hydrolyzed gave 0.57 g. 2-Ac derivative (XXI) of XI, m. 101.0-2.5° (hexane), and 1.59 g. 4-Ac derivative (XXII) of XI, m. 148-9.8° (hexane). XXI (0.85 g.) carbethoxylated, hydrogenated, and sapond. as above gave 1,1':3,3'-bis (trimethylene) ferrocene-2-propionic acid (XXIII). Cyclization of 0.72 g. XXIII with 4.0 ml. V in 20 ml.  $\text{CCl}_4$  gave only unchanged XXIII and a putative  $\beta$ -[1,1':3,3'-bis (trimethylene) ferrocenyl] ethyl trifluoromethyl ketone. Treatment (2 hrs.) of 0.5 g. XXII with 7 ml. polyphosphoric acid at various temperatures (0.65°) gave no reaction; at higher temperatures (85°), increasing amounts tar with correspondingly decreasing amounts XXIII were observed. Crude XXII converted with  $\text{PCl}_5$  into acid chloride and the latter refluxed 3 hrs. with  $\text{AlCl}_3$  in  $\text{CH}_2\text{Cl}_2$  gave only recovered XXIII. XXII (1.635 g.), 8.4 millimoles NaH, and 1.20 g. IV in 120 ml. xylene refluxed and stirred 21 hrs. under N, the resulting crude  $\beta$ -keto ester (1.81 g.) hydrogenated over 1.0 g.  $\text{PtO}_2$  at 40 psi, and the reduced ester sapond. gave 1.2 g. crude 1,1':3,3'-bis(trimethylene)-ferrocene-4-propionic acid (XXIV), oil. XXIV (1.266 g.) cyclized with 10.0 g. V in 40 ml.  $\text{CCl}_4$ , the crude product (1.10 g.) chromatographed on  $\text{Al}_2\text{O}_3$ , and the column eluted with 2 percent  $\text{Et}_2\text{O}$  in Skellysolve B gave 0.36 g. 4,4'-( $\alpha$ -oxotrimethylene)-1,1':3,3'-bis (trimethylene) ferrocene (XXV), m. 184-6° (sublimation in vacuo); further elution with 5 percent  $\text{Et}_2\text{O}$  in Skellysolve B gave 0.44 g. 4,5-( $\alpha$ -oxotrimethylene)-1,1':3,3'-bis (trimethylene) ferrocene (XXVI), m. 165.5-7.0° (sublimation in vacuo). XXV (0.132 g.), 0.83 g.  $\text{AlCl}_3$ , and 0.15 g.  $\text{LiAlH}_4$  in 60 ml.  $\text{Et}_2\text{O}$  stirred 1 hr. at room temperature, the reduction product chromatographed on  $\text{Al}_2\text{O}_3$ , and the column eluted with Skellysolve B gave 0.118 g. XX, m. 144-50° (sublimation in vacuo). Similar reduction of XXVI with  $\text{LiAlH}_4$ - $\text{AlCl}_3$  gave quantitative 1,1':3,3':4,5 -tris (trimethylene) ferrocene (XXVII), m. 160.0-2.5° (sublimation in vacuo or hexane). III (0.400 g.), 5.16 millimoles NaH, and 0.608 g. IV in 250 ml. anhydrous  $\text{C}_6\text{H}_6$  refluxed 75 hrs. under N, the whole cooled, treated with absolute EtOH followed by ice and HCl, the phases separated, the aqueous phase extracted



with  $\text{Et}_2\text{O}$ , the combined organic solutions washed with  $\text{H}_2\text{O}$  aqueous  $\text{NaHCO}_3$ , and  $\text{H}_2\text{O}$ , dried, evaporated (rotary evaporator), the residual crude di- $\beta$ -oxo ester (0.83 g.) hydrogenated in  $\text{AcOH}$  over 1.0 g.  $\text{PtO}_2$  at 39 psi, and the resulting reduced ester (0.48 g.) refluxed with 0.1 N  $\text{NaOH}$  in 3:2  $\text{EtOH-H}_2\text{O}$  gave 0.30 g. 1,1'-trimethyleneferrocene-3,4'-dipropionic acid (XXVIII), m.  $152-6^\circ$  (decomposition). XXVIII (90 mg.), 75 ml.  $\text{CCl}_4$ , and 1.0 g. V stirred 4 hrs. at room temperature in a tightly stoppered flask, poured into excess aqueous  $\text{NaHCO}_3$ , the organic phase separated, extracted repeatedly with aqueous  $\text{NaHCO}_3$ , the combined aqueous  $\text{NaHCO}_3$ , the combined aqueous  $\text{NaHCO}_3$  solutions acidified to pH 4 with  $\text{HCl}$ , extracted with  $\text{Et}_2\text{O}$ , the extract washed with  $\text{H}_2\text{O}$  to pH 5, dried, concentrated, and the residual oily oxo acid (60 mg.) hydrogenated over 50 mg.  $\text{PtO}_2$  at 40 psi gave 57.8 mg. crude XXIV, oil. Crude XXIV, 50 ml.  $\text{CCl}_4$ , and 578 mg. V stirred 4 hours at room temperature, poured into excess aqueous  $\text{NaHCO}_3$ , the phases separated, the aqueous phase extracted with  $\text{CH}_2\text{Cl}_2$ , the combined organic solutions washed with N  $\text{KOH}$ , aqueous  $\text{NaHCO}_3$ , and  $\text{H}_2\text{O}$  until neutral, dried, concentrated, and the residual oil (42.1 mg.) chromatographed on acid-washed  $\text{Al}_2\text{O}_3$  gave 11.3 mg. crude XXV, m.  $157-61^\circ$ , and 10 mg. XXVI, m.  $163-5^\circ$  (pentane). XX (0.250 g.) acetylated as above with 0.166 g.  $\text{Ac}_2\text{O}$  and 0.228 g.  $\text{AlCl}_3$  in 25 ml. dry  $\text{CH}_2\text{Cl}_2$ , the whole stirred overnight under N, and hydrolyzed with ice- $\text{H}_2\text{O}$  gave 0.234 g. 3-Ac derivative of XX, m.  $119.0-20.0^\circ$  (hexane), and 3 percent 3,3'- or 3,5-di-ac derivative of XX, m.  $176-83^\circ$ . XXVII (0.361 g.) acetylated as above with 0.24 g.  $\text{Ac}_2\text{O}$  and 0.31 g.  $\text{AlCl}_3$  in  $\text{CH}_2\text{Cl}_2$  gave 0.177 g. mixture XXIX of 2- (XXX) and 2'-Ac derivative (XXXI) of XXVII together with a little 3-Ac derivative (XXXII)



of XXVII, 0.14 g. 4'-Ac derivative of XXVII, m.  $139.5-42.0^\circ$  (hexane), and 25.0 mg. 2,2'- or 2,4'-di-Ac derivative of XXVII, m.  $124-40^\circ$  (hexane). Rechromatography of XXIX on  $\text{Al}_2\text{O}_3$  gave XXXII, m.  $108-12^\circ$ , and an inseparable 4:3 mixture of XXX and XXXI, oil. The infrared, ultraviolet, and nuclear magnetic resonance spectral characteristics of the ferrocenes were tabulated.

344. Rosenblum, M., Howells, W. G., Banerjee, A. K., and Bennett, C.,  
FERROCENE. VI. MECHANISM OF THE ARYLATION REACTION, American Chemical Society Journal, Vol. 84, 1962, pp. 2726-2732 (cf. CA 57, 862d).

Reaction of ferrocene (I) with aryldiazonium salts prepared from  $\text{PhNH}_2$  (II),  $4\text{-H}_2\text{NC}_6\text{H}_4\text{COMe}$  (III), and  $4\text{-H}_2\text{NC}_6\text{H}_4\text{OMe}$  (IV) yields not only mono- and 1,1'-diarylferrocene, but also 1,2- and 1,3-diarylferrocene. A mechanism involving internal rearrangement of a I diazonium charge-transfer complex is proposed. A solution of diazotized II, prepared from 15 g. II, 11.6 g.  $\text{NaNO}_2$ , and 25.8 g. concentrated  $\text{H}_2\text{SO}_4$ , is treated at  $0^\circ$  20 hrs. with 2 g. I and an aqueous solution of ferricinium chlorid (V), prepared from 15 g. I and 20 g.  $\text{FeCl}_3$  in anhydrous  $\text{Et}_2\text{O}$ . The mixture is decomposed with excess  $\text{NaHSO}_3$  solution and extracted with  $\text{Et}_2\text{O}$ . After washing and drying ( $\text{MgSO}_4$ ), the  $\text{Et}_2\text{O}$  layer is treated again with excess  $\text{FeCl}_3$  to yield V, which is extracted into  $\text{H}_2\text{O}$ . After decomposition with  $\text{NaHSO}_3$ , extraction with  $\text{Et}_2\text{O}$ , and evaporation of the  $\text{Et}_2\text{O}$ , the residue is dissolved in 100 ml. petr. ether and placed on a  $\text{Al}_2\text{O}_3$  column. Elution with petr. ether yields 900 mg. phenylferrocene, m.  $112\text{-}14^\circ$ , 450 mg. 1,2-diphenylferrocene, m.  $108.5\text{-}10^\circ$ , 260 mg.  $\alpha$ -biphenylferrocene, m.  $131.5\text{-}2.5^\circ$ , 1.03 g. 1,1'-diphenylferrocene, m.  $156\text{-}7^\circ$ , 70 mg.  $\alpha'$ -biphenylferrocene, m.  $128\text{-}30^\circ$ , and impure 1,3-diphenylferrocene. Similarly, employing 67.5 g. III yields 1.76 g. p-methoxyphenylferrocene, m.  $108\text{-}10^\circ$ , 40 mg.  $\alpha$ -(4-methoxyphenyl)-4-methoxyphenylferrocene, m.  $154\text{-}5^\circ$ , 1.07 g. 1,2-bis (p-methoxyphenyl) ferrocene, m.  $119\text{-}21^\circ$ , 1.13 g. 1,1'-bis (p-methoxyphenyl) ferrocene, m.  $172\text{-}4^\circ$ , and 60 mg. 1,3-bis (p-methoxyphenyl) ferrocene, m.  $159\text{-}61^\circ$ . Similarly, 34 g. IV is converted into 2.5 g. p-acetylphenylferrocene, m.  $174\text{-}5^\circ$ , 150 mg. 1,2-bis (p-acetylphenyl) ferrocene, m.  $146\text{-}7^\circ$ , 1.0 g. 1,1'-bis (p-acetylphenyl) ferrocene, m.  $243\text{-}5^\circ$ , and 1,3-bis (p-acetylphenyl) ferrocene, m.  $202\text{-}4^\circ$ .

345. Schaaf, R. L. and Lenk, C. T.,  
FERROCENES. VI. OXIDATIONS IN FRIEDEL-CRAFTS  
REACTIONS, Journal of Organic Chemistry. Vol. 28, No. 11,  
1963, pp. 3238-3240 (cf. CA 56, 14325g).

$\text{AlCl}_3$  (0.15 mole) added in 5 portions in 30 min. to 0.15 mole  $p\text{-ClCOC}_6\text{H}_4\text{COCl}$  in 100 ml. cold dry  $\text{CH}_2\text{Cl}_2$  (ice bath) under N and the mixture stirred 2 hrs. (ice bath) with gradual addition of 0.05 mole ferrocene (I) in 50 ml. dry  $\text{CH}_2\text{Cl}_2$ , the mixture kept 16 hrs. and stirred 30 min. with 100 ml. MeOH, poured into 250 ml.  $\text{H}_2\text{O}$  and washed once with  $\text{CHCl}_3$ , the purple aqueous layer shaken with Zn dust, and the colorless filtered solution extracted with  $\text{CHCl}_3$  yielded 57 percent I. With  $p\text{-O}_2\text{NC}_6\text{H}_4\text{COCl}$ , 47 percent I was recovered by reduction of the aqueous layer. I (0.02 mole) and 0.05 mole acyl chloride  $\text{RCOCl}$  (II,  $\text{R} = \text{Cl}_3\text{C}$ ) in 40 ml. dry  $\text{CH}_2\text{Cl}_2$  at  $-30^\circ$  treated in 5 min. with 0.05 mole  $\text{AlCl}_3$  in 3 portions and the mixture kept 2 hrs. at  $<20^\circ$ , poured into ice- $\text{H}_2\text{O}$  and stirred 5 min., the organic layer extracted 3 times with  $\text{H}_2\text{O}$ , and the combined aqueous solutions reduced with Zn dust, filtered, and extracted with  $\text{CHCl}_3$  yielded 37 percent I. Similar reaction with II ( $\text{R} = \text{EtO}_2\text{C}$ ) yielded 64 percent I. In the same way II ( $\text{R} = \text{ClCH}_2$ ,  $\text{Cl}_2\text{CH}$ ) gave I in 32, and 47 percent yields, but oxidation was insignificant with II ( $\text{R} = p\text{-FC}_6\text{H}_4$ , Ph, and Pr). It was suggested that the acylium ion formed from II and  $\text{AlCl}_3$  may remove an electron from I to form the ferricinium ion  $(\text{C}_{10}\text{H}_{10}\text{FE})^+$  in competition with the acylation, and that the formation of the ion is a major reaction if the acylium ion is sufficiently positive. All the cited oxidizing II have electron-withdrawing groups adjacent to the  $\text{COCl}$  group and should produce an acylium ion more electron-deficient than that of a simple acyl halide. Major oxidation was also observed with  $\text{ClCH}_2\text{CH}(\text{OEt})_2$  (III). III (0.1 mole) added dropwise in 80 min. to 0.05 mole I and 0.10 mole  $\text{AlCl}_3$  in 65 ml. ( $\text{CH}_2\text{Cl}_2$ ) at  $-20^\circ$  (N atm.) and kept 30 min., warmed to  $-5^\circ$ , and added to ice- $\text{H}_2\text{O}$ , the aqueous layer extracted with  $\text{CHCl}_3$ , and the combined organic layers evaporated, the residue (5.92 g.) extracted 6 times with 20 ml. petr. ether and each extract chromatographed on 180 g.  $\text{Al}_2\text{O}_3$ , eluted with petr. ether to yield 19 percent I, and elution continued with the usual solvents gave distinct oily fractions containing monosubstituted ferrocenes, according to infrared determinations. The aqueous layer reduced with Zn-dust and the filtered solution extracted with  $\text{CHCl}_3$ , the extract evaporated, and the moist solid

extracted with MeOH gave a residue of 33 percent crude I. The MeOH extract evaporated and the residue (2.73 g.) chromatographed yielded 4 percent I and 1.05 g. monosubstituted I, m. 14-21°,  $\lambda$  9, 10  $\mu$ . The order of addition was not critical; thus, addition of I to the Perrier complex from II (R = Cl<sub>2</sub>CH) gave 47 percent ferricinium ion, and addition of AlCl<sub>3</sub> to a mixture of I and II (R = Cl<sub>2</sub>CH) yielded 37-48 percent ferricinium ion. SOCl<sub>2</sub> (0.658 mole) and 0.263 mole p-FC<sub>6</sub>H<sub>4</sub>CO<sub>2</sub>H refluxed 7 hrs. in 25 ml. C<sub>6</sub>H<sub>6</sub> and volatile material evaporated in vacuo, the residue taken up in 90 ml. dry CH<sub>2</sub>Cl<sub>2</sub> and treated with 0.233 mole powdered anhydrous AlCl<sub>3</sub>, the mixture cooled (ice bath) and treated dropwise in 1.5 hrs. with 0.093 mole I in 90 ml. CH<sub>2</sub>Cl<sub>2</sub>, stirred 16 hrs. at 20°, and poured onto ice, stirred 4 hrs., and the aqueous phase extracted with CHCl<sub>3</sub>, the combined organic phases washed (H<sub>2</sub>O, 5 percent aqueous NaOH), the dried solution evaporated in vacuo, and the residue crystallized from 150 ml. PhMe yielded 76 percent 1, 1'-bis (p-fluorobenzoyl) ferrocene, m. 129.0-30.5°,  $\lambda$  472, 350, 250 m $\mu$  (log  $\epsilon$  2.83, 3.29, 4.28). Treatment of I with AlCl<sub>3</sub> and PrCOCl according to Vogel, et al. (CA 52, 7295f), yielded 77 percent 1, 1'-dibutyrylferrocene, m. 73.0-4.5°.

346. Shih, S., Sung, H., and Li, F.,  
TRANSLATIONS ON COMMUNIST CHINA'S SCIENCE AND  
TECHNOLOGY, NO. 156, 5. SYNTHESIS AND CERTAIN  
REACTIONS OF P. TOLYLFERROCENE (Foreign Title Not  
Available), Translated into English from Chinese by Joint  
Publications Research Service, Washington, D.C., Report  
No. JPRS-29037, TT-65-30464, N65-20576, N65-20578-10-06,  
9 March 1965, pp. 33-35.

Not abstracted.

B. Olefinic Ferrocene Derivatives and Alcohols  
in the Ferrocene Series

347. Lorkowski, H. J.,  
FERROCENE DERIVATIVES. II. THE REACTION OF  
HYDROXYALKYLFERROCENES WITH ISOCYANATES,  
Journal fuer Praktische Chemie, Vol. 23, No. 1-2, 1964,  
pp. 98-103 (cf. CA 59, 4050a).

A MePh solution containing 4.32 g. hydroxymethylferrocene (I) and 2.38 g. PhNCO was sealed in a flask with a CaCl<sub>2</sub> tube. The solvent was removed in vacuo after 48 hrs. to give 5.15 g. yellow crystals of the expected N-phenylurethan, m. 114-15° (hexane). The analogous N-methylurethan, m. 110-11°, was prepared in a similar manner from MeNCO. Heating a MePh solution containing 2.16 g. I and 1.19 g. PhNCO at 100° 3 hrs. gave, after removal of the solvent in vacuo and treatment of the oily residue with EtOH, 1.5 g. yellow crystals. Elution of the latter with C<sub>6</sub>H<sub>6</sub>-Me<sub>2</sub>CO on a neutral Al<sub>2</sub>O<sub>3</sub> column gave 0.7 g. yellow N, N-bis (ferrocenylmethyl) aniline (II), m. 165-6° (from EtOH), and 0.2 g. an unidentified yellow species, m. 153°, having the composition C<sub>24</sub>H<sub>22</sub>FeN<sub>3</sub>. PhNH<sub>2</sub> and benzanilide were also separated from the product mixture. Impure samples of a tertiary amine analogous to II were obtained by a similar reaction between α-hydroxyethylferrocene and PhNCO. The reaction between I and MeNCO gave only the urethan under all conditions tried. Heating a MePh solution containing 3.02 g. 1,1'-bis (α-hydroxyisopropyl) ferrocene (III) and 2.38 g. PhNCO at 100° 3 hrs. gave, on cooling, a white precipitate of (PhNH)<sub>2</sub>CO. A small amount of a polymer of III was isolated from the mother liquor. A mixture of 10 g. trimethylferrocenylammonium iodide, 5.48 g. p - ClC<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>, and 20 ml. H<sub>2</sub>O was heated at 100° 1.5 hrs., cooled, and extracted with C<sub>6</sub>H<sub>6</sub>. The C<sub>6</sub>H<sub>6</sub> extract was washed with dilute HCl, NaHCO<sub>3</sub> solution, and H<sub>2</sub>O, and dried. Removal of the solvent in vacuo gave 6.8 g. p-chloroanilinomethylferrocene (IV), m. 122-4° (hexane). A mixture of 4.32 g. I, 6.5 g. IV, and 2.38 g. PhNCO in MePh was heated at 100° 3 hrs. Removal of the solvent in vacuo gave a yellow residue from which 0.5 g. N, N-bis (ferrocenylmethyl)-p-chloroaniline, m. 173-5° (EtOH), was isolated by a combination of column and thin-layer chromatography. A mechanism is suggested for the formation of tertiary amines from isocyanates and hydroxyalkylferrocenes.

PART I. THE ADDITION OF CARBOXYLIC ACIDS TO DIVINYLFERROCENE. PART II. THE REACTION OF FERROCENE WITH TIN (IV) CHLORIDE IN CHLOROFORM, University Microfilms (Ann Arbor, Michigan) Order No. 65-1561, 140 pp., Dissertation Abstract, Vol. 25, No. 10, 1965, pp. 5565-5566.

#### PART I

The acetylation of ferrocene by acetic anhydride in the presence of boron trifluoride catalyst was investigated. Solutions of ferrocene and acetic anhydride were prepared in methylene chloride and then saturated with boron trifluoride. The reaction products were separated by chromatography on activity III alumina and then identified. The results revealed that ferrocene may be either mono- or diacetylated depending on the molar ratio of reactants used. A 1:1 molar ratio of acetic anhydride to ferrocene gave almost exclusive monacetylferrocene, whereas with increasing ratios of anhydride to ferrocene increasing amounts of diacetylferrocene were found.

Divinylferrocene was prepared in 45 percent yield by dehydration of bis (1-hydroxyethyl) ferrocene. The dehydration was accomplished by dispersing the biscarbinol on activity I basic alumina and heating at 205°C for 90 seconds at a pressure of 50 mm. of Hg. Uniform heat transfer was attained by rapidly rotating the flask while heating. After extraction of the alumina with petroleum ether, the divinylferrocene was isolated by chromatography on activity III alumina. Divinylferrocene is a low melting solid (41-42°C), possessing the characteristic odor of alkyl ferrocenes.

As expected, divinylferrocene readily underwent an electrophilic addition reaction with absolute acetic acid. The product, bis (1-acetoxylethyl) ferrocene, was identical to that prepared by the reaction of bis (1-hydroxyethyl)-ferrocene and acetic anhydride in the presence of pyridine. With adipic acid, divinylferrocene formed a polymer, but this polymer did not contain the adipate group.

#### PART II

The reaction between ferrocene and tin (IV) chloride in chloroform was investigated. The product from the reaction has an empirical formula of  $C_{20}H_{20}Fe_2Sn_3Cl_{12}$ . The

reaction is an oxidation-reduction one in which ferrocene is oxidized to ferricinium ion and part of the tin (IV) is reduced to tin (II). The infrared, visible, and ultraviolet spectra of both the solid material and in solution were identical to that of known ferricinium salts. Likewise, the paramagnetic moment of the material was in agreement with that reported for the ferricinium ion. Ion-exchange on cationic resin and precipitation with large anions also indicated the presence of the ferricinium ion which is the cation in the material.

The results of experiments on anionic exchange resin indicated that at least one-half of the tin is in the anionic form, probably as the chloro anionic complexes since chloride ion was found associated with the anionic tin. The far infrared spectrum of the solid  $C_{20}H_{20}Fe_2Sn_3Cl_{12}$  material revealed several absorption bands which could be attributed to the hexachlorostannate (IV) and trichlorostannate (II) ion. One-third of the total tin was found in the  $+2$  oxidation state and in the anionic form. From the data it appears that the hexachlorostannate (IV) ion and the trichlorostannate (II) ion in the molar ratio of 1:2 are the anions in the material. The disposition of the remaining tin, which is in the  $+4$  oxidation state, is open to question, but may be associated with the anionic tin as polynuclear anionic complexes.

349. Nesmeyanov, A. N. and Kritskaya, I. I.,  
FORMATION OF ETHERS OF FERROCENEMETHANOLS  
AND THEIR HYDROLYSIS UNDER THE CONDITIONS OF  
ADSORPTION CHROMATOGRAPHY, Izvestiya Akademii Nauk  
SSSR, Seriya Khimicheskaya, No. 12, December 1964, pp.  
2160-2165.

This is a detailed study of the etherification of ferrocenyl carbinols in the presence of silica. The weakly acidic silica catalyses etherification under very mild conditions and liberated water is bound by silica. The silica surface is a convenient medium for the etherification of ferrocene methanols.

350. Nesmeyanov, A. N. and Kritskaya, I. I.,  
FORMATION OF ETHERS OF FERROCENYL CARBINOLS  
AND THEIR HYDROLYSIS UNDER CONDITIONS OF  
ADSORPTIONAL CHROMATOGRAPHY, Izvestiya Akademii  
Nauk SSSR Seriya Khimicheskaya, No. 12, 1964, pp. 2160-  
2165, (cf. CA 58 7971e) (In Russian).

It was shown that ferrocenylcarbinols (I) can be etherified only in the presence of acid catalysts; a  $\text{SiO}_2$  surface used for chromatography is a convenient means for such etherification. Keeping the carbinol in ROH on  $\text{SiO}_2$  2 days gave the following phenylferrocenyl R ether (R shown): Me, m. 113-14°; Et, m. 55-5.5°; iso-Pr, m. 74.5-5.5°; and 1,1'-bis ( $\alpha$ -hydroxybenzyl) ferrocene di-R ether (R shown): Me, m. 139-40°; Et, m. 107-7°. The yields were 83-98 percent. Shaking I with ROH 0.5 hr. in the presence of  $\text{SiO}_2$  was also effective. The first procedure also gave 20 percent bis (phenylferrocenyl) methyl ether, m. 142-3°; the carbinol heated with p-MeC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>Cl in C<sub>6</sub>H<sub>6</sub> gave 84 percent while with KHSO<sub>4</sub>, 83.9 percent yields. When benzoylferrocene was reduced with LiAlH<sub>4</sub> and the mixture treated with HCl, the same ether was formed in varying yields. Also formed in this reaction was C<sub>34</sub>H<sub>30</sub>Fe<sub>2</sub>O, m. 111-12°, which was one of stereoisomeric forms. Benzoylferrocene was converted by a Grignard reaction into diphenylferrocenylcarbinol, m. 137-8°, which was unchanged by heating with MeOH, while with AcOH catalyst in 40 min. at room temperature 80.7 percent phenylferrocenyl carbinyl Me ether (II), m. 110.5-12°, was formed; similarly was prepared. 63 percent Me diphenylferrocenylcarbinyl ether, m. 98-9°. II heated in dioxane with 50 percent AcOH 2 hrs. gave 20 percent unchanged ether, 56 percent benzoylferrocene, and some mixed stereoisomers of diphenyldiferrocenylethane, m. 204-60°. The methyl ether of methylferrocenylcarbinol under these conditions gave 66 percent methylferrocenylcarbinol, m. 74-6°, and 2.3 percent vinylferrocene, m. 48-50°. Me phenylferrocenylcarbinyl ether in 2 hrs. at 60-5° in 30 percent H<sub>2</sub>SO<sub>4</sub> gave 94.4 percent mixed isomers of diphenyldiferrocenylethane. Similarly, bis (phenylferrocenylcarbinyl) ether gave 73 percent diphenyldiferrocenylethane isomers, m. 220-60°, and some free carbinols, m. 78-80. The ethers of ferrocenylcarbinols were also hydrolyzed in several hrs. of contact with chromatographic Al<sub>2</sub>O<sub>3</sub> in heptane.



351. Purdue University, Lafayette, Indiana,  
CHEMISTRY OF FERROCENE AND RELATED COMPOUNDS,  
FINAL REPORT by R. A. Benkeser, January 1963, Report No.  
AFOSR 4498, AD-600 969, Contract No. AF49 638 297  
(Unclassified Report).

Researches on the following areas of study are summarized: Electrical effects in ferrocene; addition reactions of vinylferrocene; and alkylferrocene metalation.

352. Purdue University, Lafayette, Indiana,  
THE METALATION OF DIPHENYLFERROCENYLCARBINOL  
by R. A. Benkeser, W. P. Fitzgerald, and M. S. Melzer, Report  
No. AFSOR TN60 1365, AD-246 801, Contract No. AF49 638  
297 (Unclassified Report).

Not abstracted.

353. Schlogel, K. and Egger, H.,  
SYNTHESIS AND REACTION OF FERROCENYLACETYLENE,  
Monatshefte, Vol. 94, No. 2, 1963, pp. 376-392.

Refer to item No. 219 for abstract.

### C. Acyl Ferrocene Derivatives

354. Air Force Materials Laboratory, Air Force Systems Command,  
Wright-Patterson Air Force Base, Ohio,  
THE PHOTOCHEMICALLY INDUCED FRIES REARRANGEMENT  
OF AROMATIC ESTERS by J. J. Mattice, December 1964,  
Report No. ML-TDR-64 170, AD-610 403, (Unclassified  
Report).

This investigation involved aryl esters for which a photochemical rearrangement had not previously been reported. Results of the photolysis of eight aromatic benzoates (phenyl, p-tolyl, p-chlorophenyl, phenyl pchloro, 2,6-dimethylphenyl, mesityl, and phenyl mesitoate, are presented. Ortho- and para-hydroxybenzophenones are formed in cases where structural considerations permit, as well as products which, in certain instances, could not be identified.

The photo-reaction has also been studied in two examples in the ferrocene series. An unexpected preference for formation

of para-hydroxyketone is observed. The photo-fries reactions investigated are discussed on the basis of the products formed and in comparison with related work in the current literature. Possible intermediates and mechanisms which might account for the observed reactions are pointed out and suggestions for future experimental work outlined.

355. Asbury, R. L., Jr.,  
THE ACID-CATALYZED REACTIONS OF SELECTED  
 $\beta$ -FERROCENYLPROPIONIC ACIDS, University Microfilms  
(Ann Arbor, Michigan) Order No. 65-9529

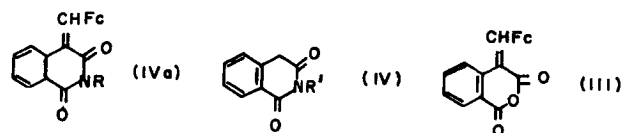
Refer to item No. 152 for abstract

356. Belder, A. N., de Bourne, E. J., and Pridham, J. B.,  
CONDENSATION OF FERROCENEALDEHYDE WITH D-  
GLUCITOL AND D-MANNITOL, Chemical Society Journal,  
December 1964, pp. 5486-5488.

The cyclic acetals of ferrocenecarbaldehyde with D-glucitol and D-mannitol were prepared.

357. Boichard, J., Monin, J. P., and Tirouflet, J.,  
METALLOCENES. I. IMINES AND CHALCONES DERIVED  
FROM FERROCENECARBOXALDEHYDE AND ACETYL-  
FERROCENE, Société Chimique de France Bulletin, No. 4,  
1963, pp. 851-856.

Ferrocene (FcH) (10 g.) treated according to Broadhead, et al. (CA 52, 18359c) with 14.7 g. HCONMePh and 16.7 g. POCl<sub>3</sub> gave 6 g. ferrocenecarboxaldehyde (I), m. 124-5°; semicarbazone m. 240-2°; thiosemicarbazone m. 190-1° (decomposition). I and an equimolar amount of RNH<sub>2</sub> in a min. of absolute alcohol kept 1 to 30 days at 0° with gradual precipitation of the aldimine and the product crystallized (petr. ether) gave FcCH: -N<sup>R</sup> (Fc = ferrocenyl) (II) (R and m. p. given): Ph, 77°;  $\alpha$ -C<sub>10</sub>H<sub>7</sub>, 128°;  $\beta$ -C<sub>10</sub>H<sub>7</sub>, 106°; 2-thiazolyl, 128°. I and an equimolar amount of homophthalic anhydride in AcOH containing several drops of Ac<sub>2</sub>O refluxed and the precipitate crystallized (Ac<sub>2</sub>O) gave the condensation product (III), m. 189. I and equimolar amounts of homophthalimides (IV) refluxed in absolute alcohol with several drops of piperidine and the precipitate recrystallized from alcohol gave 40-60 percent IVa (R and m. p. given): H, 240°; Me, 182°; Ph,



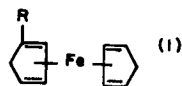
234°. All homophthalimides were dark violet and were only obtained in one stereoisomeric form. I (0.5 g.), 0.35 g. indan-1,3-dione (IVb), and several drops of piperidine refluxed in 15 ml. absolute alcohol and the precipitate recrystallized from alcohol gave 0.35 g. blue-black needles of 2-FcCH derivative of IVb, m. 167-8°. FcLi (freshly prepared from 28 g. FcH) in dry Et<sub>2</sub>O at -20° treated gradually in 30 min. with 30 g PhCH<sub>2</sub>ONH<sub>2</sub> in 70 ml. dry Et<sub>2</sub>O, the mixture stirred (N atm.) 30 min. at 25° and treated at -10° with 500 ml. 10 percent HCl, the Et<sub>2</sub>O layer washed with 300 ml. 10 percent HCl, the acid layers combined and neutralized, the product purified by repeated acidification and neutralization, and the powder (7.1 g., m. 130°) sublimed at 70-95°/2mm. and further at 130-150°/2 mm gave 2.5 g. ferrocenylamine, FcNH<sub>2</sub> (V), m. 157-8°, and a second product, ferrocenyl-1,1'-diamine. V treated with Ac<sub>2</sub>O in the presence of fused NaOAc and the product crystallized from Et<sub>2</sub>O-petr. ether gave FcNHAc, m. 170°. V and an equimolar amount of α-furoyl chloride heated 1 hr. on a steam bath in C<sub>5</sub>H<sub>5</sub> and the hydrolyzed mixture extracted with CHCl<sub>2</sub> gave a very small yield of N-(α-furoyl)ferrocenylamine, m. 151-2° (MeOH), solidifying and m. 161-2°. V (0.5 g.) and 2.8 g. 2-formylthiophene kept 72 hrs. at 20° in 20 ml. absolute alcohol and the crystalline product (0.4 g., m. 120-2°) recrystallized from Et<sub>2</sub>O-petr. ether gave 0.2 g. N-(2-thenylidene)ferrocenylamine, m. 127-9°. Preparation according to Broadhead, et al. (loc. cit.) gave acetylferrocene (VI); oxime m. 184-5°; semicarbazone m. 267-7°; thiosemicarbazone m. 195-6°. Condensation of I with Me ketones and of VI with aldehydes according to method A or B gave the corresponding chalcones, FcCH: CHCOR and FcCOCH: CHR (VII and VIII). Equimolar amounts of I and the ketone in a minimum amount of alcohol treated with excess 15 percent NaOH solution, the mixture refrigerated several hrs. and diluted with a small amount of H<sub>2</sub>O, and the H<sub>2</sub>O-washed precipitate recrystallized (dilute alcohol) gave the corresponding chalcone (method A). Equimolar amounts of components in a minimum of alcohol treatment with 1-2 ml. 50 percent NaOH and the mixture kept several hrs. at 60° produced the required chalcone (method B). The m. p. and yields of VII and VIII obtained by methods A and B were tabulated.

The chalcone (0.002M), 0.01M  $\text{HONH}_2$ , HCl, and 0.05M KOH refluxed 1 hr. in 40 ml. alcohol on a steam bath, the mixture poured into ice- $\text{H}_2\text{O}$  and acidified, and the precipitate chromatographed from  $\text{Et}_2\text{O}$  on  $\text{Al}_2\text{O}_3$  gave the corresponding oximes (chalcone, oxime m.p. given): VIII (R = Ph), 120°; VII (R = Ph), 144°; VII (R = Fc), 170°. VII (R = o- $\text{HOC}_6\text{H}_4$ ) (2.1 g.) in 100 ml. alcohol refluxed 1 hr. [with gradual addition of 50 ml. Prideaux-Ward buffer (pH 6.8)], the mixture poured onto ice containing several drops of HCl, the dried precipitate taken up in  $\text{Me}_2\text{CO}$ , the solution chromatographed on  $\text{Al}_2\text{O}_3$ , and eluted with dry  $\text{Et}_2\text{O}$  and the fraction (1 g., m. 130°) recrystallized from slightly acidified dilute alcohol gave 0.7 g. 2-ferrocenyl-4-chromanone, m. 136°. Further elution with MeOH gave 1 g. starting material. The  $\text{Me}_2\text{CO}$ -insol. material, m. 215° recrystallized from  $\text{MeOCH}_2\text{CH}_2\text{OH}$  gave orange platelets of a dimeric o-hydroxychalcone. Michael condensations of the chalcones were carried out either by refluxing the compounds in alcohol (20-5 hrs.) or by carrying out the condensation at 20° (10-15 days). FcCH: CHBz (0.632 g.) in 35 ml. absolute alcohol treated with 0.5 g.  $\text{AcCH}_2\text{COMe}$  and 1.4 ml. 10 percent alcohol. NaOEt, the mixture refluxed 24 hrs., cooled, acidified with dilute HCl, and diluted with  $\text{H}_2\text{O}$ , the dried product taken up in  $\text{Me}_2\text{CO}$ , chromatographed on  $\text{Al}_2\text{O}_3$ , and eluted with  $\text{Et}_2\text{O}$ , and the product recrystallized (dilute alcohol) gave FcCH: CHAc, m. 86°, also obtained directly from 0.642 g. I in alcohol, 0.500 g.  $\text{Me}_2\text{CO}$ , and 1 ml. 20 percent NaOH kept 2 hrs. at 20° and 4 hrs. at 0°, diluted with  $\text{H}_2\text{O}$  and the precipitate recrystallized from dilute alcohol. FcCH: CHBz (0.632 g.) and 0.350 g.  $\text{AcCH}_2\text{CO}_2\text{Et}$  condensed in the presence of an equivalent amount NaOEt in absolute alcohol by refluxing 10 hrs., the colorless solution acidified and diluted with  $\text{H}_2\text{O}$ , and the precipitate dried and chromatographed on  $\text{Al}_2\text{O}_3$  gave 0.175 g. 5-ferrocenyl-3-phenyl-2-cyclohexen-1-one, m. 146°. FcCOCH: CHPh (0.632 g.), 0.35 g.  $\text{AcCH}_2\text{CO}_2\text{Et}$ , and 8 drops 40 percent Triton B in 30 ml. alcohol refluxed 26 hrs., the acidified solution diluted with  $\text{H}_2\text{O}$ , and the product chromatographed on  $\text{Al}_2\text{O}_3$  and recrystallized repeatedly from dilute alcohol gave 3-ferrocenyl-5-phenyl-6(4)-carbethoxy-2-cyclohexen-1-one, m. 143°. FcCOCH: CHPh (0.948 g.), 0.5 g.  $\text{H}_2\text{C}(\text{CO}_2\text{Et})_2$ , and 2.1 ml. 10 percent NaOEt in 50 ml. alcohol refluxed 21 hrs., the neutralized solution diluted with  $\text{H}_2\text{O}$ , the gummy product taken up in  $\text{C}_6\text{H}_6$ , chromatographed on  $\text{Al}_2\text{O}_3$ , and eluted with  $\text{Et}_2\text{O}$ , and the orange eluate evaporated gave 0.070 g. yellow needles (IX), m. 118-20°. FcCOCH: CHPh (0.948 g.), 0.5 g.

$\text{H}_2\text{C}(\text{CO}_2\text{Et})_2$ , and 0.6 ml. 10 percent alcohol NaOEt kept 2 weeks at  $20^\circ$  in alcoholic  $\text{Et}_2\text{O}$ , the mixture acidified with dilute HCl and diluted with  $\text{H}_2\text{O}$ , and the dried product chromatographed on  $\text{Al}_2\text{O}_3$  and eluted with  $\text{C}_6\text{H}_6$  gave 0.340 g IX. IX may be the normal addition product  $\text{FcCOCH}_2[\text{CH}(\text{CO}_2\text{Et})_2]\text{CH}_2\text{Ph}$ , or the rearrangement product,  $\text{FcCOCH}(\text{CH}_2\text{CO}_2\text{Et})\text{CHPhCH}_2\text{CO}_2\text{Et}$ .

358. Da Re, P. and Sianesi, E.,  
CONDENSATION REACTIONS OF FORMYL- AND  
ACETYLFERROCENE, Experientia, Vol. 21, No. 11, 1965,  
pp. 648-649.

Ferroceneacrylic acids were prepared by means of the Reformatskii and Wittig reactions. Thus, condensations of I (R = CHO) (II) and I (R = Ac) with 100 percent excess Zn and



$\text{BrCH}_2\text{CO}_2\text{Et}$  in  $\text{C}_6\text{H}_6$ -PhMe (1:1) gave  $74-5^\circ$  of I (R =  $\text{CH}:\text{CHCO}_2\text{Et}$ ) (III) and I (R =  $\text{CMe}:\text{CHCO}_2\text{Et}$ ) (IV), m.  $69-72^\circ$  (dilute EtOH), respectively. Sapon. of III and IV produced respectively I (R =  $\text{CH}:\text{CHCO}_2\text{H}$ ) (V) and I (R =  $\text{CMe}:\text{CHCO}_2\text{H}$ ) (VI), m.  $176-7^\circ$  (decomposition). V was prepared (82 percent yield) also by hydrolysis of the product obtained from the condensation of II with  $\text{Ph}_3\text{P}:\text{CHCO}_2\text{Et}$  in  $\text{C}_6\text{H}_6$ . Catalytic (Pd-C) hydrogenation of V and VI gave, respectively I (R =  $\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$ ) and I (R =  $\text{CHMeCH}_2\text{CO}_2\text{H}$ ), m.  $95-6^\circ$ ; Et ester b<sub>0.1</sub>  $125-30^\circ$ . Aldol condensation of II and  $\text{MeNO}_2$  produced 30 percent I (R =  $\text{CH}(\text{OH})\text{CH}_2\text{NO}_2$ ) m.  $114^\circ$ , and this warmed in AcOH gave 32-7 percent I (R =  $\text{CH}:\text{CHNO}_2$ ), m.  $139^\circ$ .

359. Dormond, A. and Décombe, J.,  
THE REFORMATSKY REACTION IN THE FERROCENE  
SERIES, Academie des Sciences, Comptes Rendus, Vol. 263,  
No. 2, 11 July 1966, p. 149.

Ethyl bromacetate and bromo-2-propionate in the presence of zinc react with the ketone derivatives of ferrocene, resulting in alcohol esters which can generally be dehydrated. Hydrogenation and saponification of these ethylene esters leads to new ferrocene substitution products, which can be cyclized in homoannular derivatives. One of them has given a homo-heteroannular compound which is the first of this type.

360. Duke University, Durham, North Carolina,  
ACYLATIONS OF BISACETYLFERROCENE WITH ESTERS  
BY POTASSIUM AMIDE TO FORM BIS-BETA-DIKETONES.  
CONSIDERATION OF MECHANISM by C. E. Cain, A. T.  
Mashburn, Jr., and C. R. Hauser, June 1960, Report No.  
AROD-1443-41, AD-259 178 (Unclassified Report).

Acylations at both of the methyl groups of bisacetylferrocene with esters by potassium amide in liquid ammonia to form bis-beta-diketones appears to be quite general. Unsuccessful attempts were made to isolate the corresponding mono-beta-diketones, which might be expected as intermediates. The bis-beta-diketones were allowed to react with an excess of hydrazine to form bispyrazoles. A mechanism for the diacylations is suggested.

361. Duke University, Durham, North Carolina,  
ALKALI CATALYZED ALDOL CONDENSATION OF BIS-  
ACETYLFERROCENE WITH BENZALDEHYDE TO FORM  
MONO- AND DIBENZALDEHYDE DERIVATIVES by A. T.  
Mashburn, Jr., C. E. Cain, and C. R. Hauser, April 1960,  
AROD-1443-39, AD-249 336 (Unclassified Report).

Not abstracted.

362. Furdik, M., Toma, S., Dzurilla, M., Suchy, J.,  
FERROCENE DERIVATIVES. CONDENSATION OF HALO-  
FORMS AND CHLORAL WITH SOME FERROCENE CARBONYL-  
DERIVATIVES. Chemie Zvesti, Vol. 18, 1964, pp. 607-613.

Refer to item No. 227 for abstract.

363. Huffman, J. W. and Asbury, R. L., Jr.,  
CYCLIZATION OF  $\beta$ -FERROCENYLPROPIONIC ACIDS.  
Journal of Organic Chemistry, Vol. 30, No. 11, 1965,  
pp. 3941-3943.

Cyclization of a variety of  $\beta$ -ferrocenylpropionic acids (I,  $C_{10}H_9FeCHRCH_2R'CO_2H$ ) under Friedel-Crafts conditions was known to give rise to heteroannularly substituted ketones. Suitable modification of the alkyl chain might provide acids which would undergo cyclization to give significant quantities of the homoannular indanone analogs. Accordingly I (R = Me, R' = H; R = Ph, R' = H; R = R' = Me) (II, III, IV) were prepared. Reaction of acetylferrocene under standard Reformatskii conditions gave the hydroxy esters

$C_{10}H_9FeCMe(OH)CH_2CO_2Et$  and  $C_{10}H_9FeCMe(OH)CHMeCO_2Et$ , dehydrated with  $p-MeC_6H_4SO_3H$  in  $C_6H_6$  and saponified to give  $\beta$ -ferrocenylcrotonic acid and  $\alpha$ -methylcrotonic acid. Benzoylferrocene was similarly converted to  $\beta$ -ferrocenylcinnamic acid. Hydrogenation of the unsaturated acids readily produced II, III, and IV, homogeneous by thin-layer chromatography on silica gel, presumably a mixture of erythro and threo isomers. Cyclization of II by either polyphosphoric acid or  $(CF_3CO)_2O$  gave 32 and 75 percent yields of 1, 1'-( $\alpha$ -oxo- $\alpha'$ -methyltrimethylene)ferrocene. Similarly, cyclization of III and IV gave bridged structure compounds. In these relatively simply substituted ferrocenylpropionic acid derivatives, the intramolecular Friedel-Crafts reaction gives heteroannular cyclization.

364. Nesmeyanov, A. N., Perevalova, E. G., and Beinoravichute, Z. A.,  
REDUCTION OF FERROCENECARBOXYLIC ACIDS, Doklady Akademii Nauk SSSR, Vol. 112, 1957, pp. 439-440.

Refer item No. 177 for abstract

365. Nesmeyanov, A. N., Sazonova, V. A., and Drozd, V. N.,  
THE EFFECT OF CARBOXYL AND CARBOMETHOXYL GROUPS ON SUBSTITUTION OF HALOGEN IN FERROCENE COMPOUNDS, Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, 1962, pp. 45-47 (cf. CA55, 21081g)

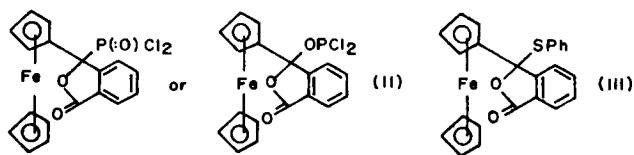
In contrast with other electron-acceptor groups,  $CO_2H$  facilitated the substitution of halogen bound to a ferrocene system. Treatment of 1'-bromo-1-acetylferrocene with iodine in pyridine overnight (heating 1.5 hrs. on a steam bath in initial stages), followed by 24 hrs. in 5 percent KOH, gave 41 percent 1'-bromo-1-ferrocenecarboxylic acid, decomposed at  $154-8^\circ$ ;  $CH_2N_2$  converted this to Me ester (I), m.  $68-9.5^\circ$ . Refluxing the free acid with aqueous alcohol  $Cu(OAc)_2$  15 min. gave 60 percent 1'-acetoxysterrocene-1-carboxylic acid, decomposed at  $126-30^\circ$ , which with  $CH_2N_2$  gave its Me ester (II), m.  $46-7.5^\circ$ . Similar treatment of I with  $Cu(OAc)_2$  30 min. gave after chromatographic separation on  $Al_2O_3$  much unreacted I and only a low yield of II.

366. Nesmeyanov, A. N., Sazonova, V. A., Romanenko, V. I., and Zol'nikova, G. P.,  
 PHOTOLYSIS OF 1,1'-FERROCENEDICARBOXYLIC ACID,  
Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 9,  
 1965, pp. 1694-1695 (In Russian).

Photolysis of the title acid in 5 percent KOH under incandescent lamplight 5 hrs. gave 96 percent cyclopentadiene-carboxylic acid dimer, m. 192°; this gave the Me ester, dimer, m. 84°, on being treated with MeOH-H<sub>2</sub>SO<sub>4</sub>. Thus the reaction resulted in rupture of Fe-C bond.

367. Nesmeyanov, A. N., Vil'chevskaya, V. D., and Kochetkova, N. S.,  
 REACTIONS OF o-CARBOXYBENZOYLFERROCENE, Doklady Akademii Nauk SSSR, Vol. 165, No. 4, 1965, pp. 835-837  
 (In Russian).

Treatment of the title compound (I) with excess PCl<sub>3</sub> overnight gave, after removal of unreacted PCl<sub>3</sub> in vacuo, 85 percent yellow needles of II, decomposed 131° (heptane). Its ir spectrum was described, but assigned structures of the



P-component could not be specifically verified by these spectral bands. II heated with aqueous AcOH gave a precipitate of inorganic Fe salts while the filtrate gave I. II and EtOH-Et<sub>3</sub>N in Et<sub>2</sub>O, mixed slowly and kept overnight, gave 70 percent Et<sub>3</sub>N.HCl while the filtrate from this gave 24 percent yellow solid, decomposed 145-6°, in which evidently 1 Cl atom had been replaced by EtO group. This product was unchanged by Et<sub>3</sub>N. I, and PhSH in H<sub>3</sub>PO<sub>4</sub> overnight, then heated to 50°, gave on dilution with ice 97 percent III, m. 144.5-45°. I and PhOH in H<sub>3</sub>PO<sub>4</sub> in 7 hrs. at 50-60° gave 3,3'-diferrrocenyl-3,3'-diphthalide, decomposed 250°, and 41 percent yellow solid, decomposed 180°, C<sub>24</sub>H<sub>18</sub>FeO<sub>3</sub>. I and PhOH or PhSH failed to react in the absence of H<sub>3</sub>PO<sub>4</sub>. II was stable to action of air, H<sub>2</sub>O, or alkali.



368. Nesmeyanov, A. N., Vol'kenau, N. A., and Bolesova, I. N.,  
LIGAND EXCHANGE IN FERROCENE, Doklady Akademii  
Nauk SSSR, Vol. 149, No. 3, 1963, pp. 615-618.

Refer to item No. 336 for abstract.

369. Nesmeyanov, A. N., Vol'kenau, N. A., Woodward, et al.,  
ACYLATION OF ACETYL- AND ETHYLFERROCENES,  
Doklady Akademii Nauk SSSR, Vol. 111, 1956, pp. 605-608  
(cf. CA 50, 15519h and CA 48, 2053g).

Refer to item No. 183 for abstract.

370. Pavlik, I. and Handlir, K.,  
DONOR-ACCEPTOR COMPLEXES OF 1,1'-DIACETYL-  
FERROCENE WITH ALUMINUM CHLORIDE, ALUMINUM  
BROMIDE AND TITANIUM CHLORIDE, Collection of  
Czechoslovak Chemical Communications, Vol. 31, No. 5,  
1966, p. 1958.

Not abstracted.

371. Petrov, A. D., Sokolova, E. B., and Bakunchik, G. P.,  
REACTION OF METHYL ESTERS OF MONO-AND DICARBOX-  
YLIC ACIDS OF FERROCENE WITH  $\alpha$ - and  $\gamma$ -HALOMAGNE-  
SIUM DERIVATIVES OF ALKYL SILANES, Doklady Akademii  
Nauk SSSR, Vol. 148, 1963, pp. 598-600.

Ferrocenemono- and -dicarboxylic acids were prepared by metalation of ferrocene with BuLi, followed by treatment with CO<sub>2</sub>; acidification gave 27 percent monocarboxylic acid and 22 percent dicarboxylic acid. These were converted respectively to Me ester, m. 114-15°, and di-Me ester, m. 69°. These were treated with Me<sub>3</sub>SiCH<sub>2</sub>MgCl and Me<sub>3</sub>Si(CH<sub>2</sub>)<sub>3</sub>MgCl in Et<sub>2</sub>O and gave (C<sub>5</sub>H<sub>5</sub>FeC<sub>5</sub>H<sub>4</sub> = ferrocenyl): 66 percent C<sub>5</sub>H<sub>5</sub>FeC<sub>5</sub>H<sub>4</sub>COCH<sub>2</sub>SiMe<sub>3</sub>, C<sub>5</sub>H<sub>4</sub>COCH<sub>2</sub>SiMe<sub>3</sub>, m. 66°; 57 percent MeO<sub>2</sub>CC<sub>5</sub>H<sub>4</sub>FeC<sub>5</sub>H<sub>4</sub>COCH<sub>2</sub>SiMe<sub>3</sub>, m. 106-8°; 90 percent C<sub>5</sub>H<sub>5</sub>FeC<sub>5</sub>H<sub>4</sub>C(OH)(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>, m. 60-2°; 87 percent Fe[C<sub>5</sub>H<sub>4</sub>C(OH)(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub>], m. 107-8°. Their structures were confirmed by the infrared spectra.

372. Rausch, M. D., Bogel, M., and Rosenberg, H.,  
DERIVATIVES OF FERROCENE. PART II. SOME REDUCTION  
PRODUCTS OF BENZOYLFERROCENE AND 1, 1-DIBENZOYL-  
FERROCENE, Charles J. Cleary Awards for Papers on  
Material Sciences, Washington, D. C., Library of Congress,  
Science and Technology Division, 1962, pp. 117-120 (N63-  
13234 07-01).

The reduction of benzoyl- and 1, 1'-dibenzoylferrocene to benzyl- and 1, 1'-dibenzoylferrocene has been accomplished by either catalytic hydrogenation or by reduction with sodium and ethanol. 1-Hydroxybenzylferrocene has been prepared by the sodium borohydride reduction of benzoylferrocene, while the reduction of 1, 1'-dibenzoylferrocene with lithium aluminum hydride has produced 1, 1'-di (1-hydroxybenzyl) ferrocene. The action of a number of other reducing agents on these aryl ferrocenyl ketones is discussed.

373. Rinehart, K. L., Jr., Curby, R. J., Jr., Gustafson, D. H.,  
Harrison, K. G., Bozak, R. E., and Bublitz, D. E.,  
ORGANIC CHEMISTRY OF FERROCENE. V. CYCLIZATION  
OF  $\omega$ -FERROCENYLALIPHATIC ACIDS, American Chemical  
Society Journal, Vol. 84, 1962, pp. 3263-3269, Acta Chemica  
Scandinavica, Vol. 16, 1962, p. 1199 (CA 57, 5850g)

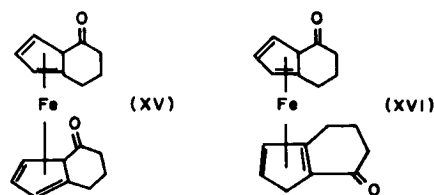
The effect of chain length on cyclization was investigated in a series of  $\omega$ -ferrocenylaliphatic acids. Ferrocenylacetic acid (I) (50 mg.) and a large excess polyphosphoric acid (Ia) heated 19 hrs. at 40° with occasional manual stirring (small samples of the mixture were removed from time to time, decomposed, with ice H<sub>2</sub>O, and equilibrated between aqueous NaHCO<sub>3</sub> and Et<sub>2</sub>O) gave only unchanged I. The same reaction carried out at 56° gave no neutral product and resulted in decomposition. Acetylferrocene (II) (58.7 g.) in 500 ml. anhydrous C<sub>6</sub>H<sub>6</sub> added dropwise during 90 min. to 60.7 g., (EtO)<sub>2</sub>CO (III), 23.9 g. 51.8 percent NaH-mineral oil dispersion, and 200 ml. C<sub>6</sub>H<sub>6</sub> with stirring, the mixture refluxed 24 hrs. under N, cooled, treated with 25 ml. absolute EtOH, poured over ice containing a slight excess aqueous layer extracted with C<sub>6</sub>H<sub>6</sub> until the extract was colorless, the combined C<sub>6</sub>H<sub>6</sub> solutions washed with H<sub>2</sub>O, dried, evaporated (rotary evaporator), the residual biphasic oil kept 2 hrs. at room temperature, and the resulting solid separated by decanting residual III gave 64 g. Et ferrocenoylacetate (IV), m. 49-53°. The above carbethoxylation carried out in 500 ml.

EtO with 60.7 g. III, 23.9 g. NaH-mineral oil dispersion, and 58.7 g. II, the mixture worked up, the resulting red oil chromatographed on 500 g. Florex in a minimum amount  $C_6H_6$ , the column developed and eluted with 1:1  $C_6H_6$ -cyclohexane, the first fraction evaporated (rotary evaporater), the residual oil (55.5 g.) rechromatographed over the same Florex column (after the column had been washed with MeOH followed by  $C_6H_6$ ), and the column eluted with 50 percent  $Et_2O$  in  $C_6H_6$  gave 5.0 g. 1,3-diferrocenyl-2-buten-1-one (V), m. 123-4° (hexane); the second fraction from the column evaporated (rotary evaporator) gave 13.4 g. IV, m. 49-51°. II carbethoxylated by  $NaNH_2$  in liquid  $NH_3$  gave IV, which was contaminated with 2 crystalline forms of  $HN(CO_2Et)_2$ , m. 51-2° and 74-5°. V (388 mg.) in 100 ml.  $Et_2O$  added dropwise to 1 millimole MeMgI in 40 ml. absolute  $Et_2O$  under Ar with stirring, the blue solution refluxed 6 hrs. cooled, hydrolyzed with saturated aqueous  $NH_4Cl$ , and worked up gave 415 mg. crude unchanged V; crude V chromatographed on  $Al_2O_3$  (a single band was obtained) and eluted with  $Et_2O$  gave V, m. 124-6.5°. V (190 mg.) and 4 millimoles MeMgI in  $Et_2O$  treated as above, the blue solution kept overnight at room temperature, the  $Et_2O$  distilled, the residual blue solid treated with tetrahydrofuran, the solution heated 7 hrs. under reflux (52°), cooled, and worked up as above gave only 169 mg. crude unchanged V. IV (13.4 g.) in 150 ml. AcOH containing 2.0 g.  $PtO_2$  (prereduced in situ) stirred 45 hrs. under H at room temperature and atm. pressure larger amounts IV (50-100 g.) were hydrogenated 48-72 hrs. at room temperature and 200 psi with comparable results, the catalyst filtered off, the filtrate diluted with  $H_2O$ , treated with a small amount ascorbic acid, and the product isolated by repeated extraction with  $Et_2O$  gave 11.9 g. crude  $\beta$ -ferrocenylpropionic acid (VI) Et ester (VII), oil. Crude VII refluxed 2 hrs. in 0.5N NaOH in 50 percent EtOH, the solution cooled, diluted with  $H_2O$ , extracted with  $Et_2O$ , cooled in an ice bath, and acidified to pH3 with aqueous HCl gave 9.50 g. VI, m. 119-20°. VI (9.50 g.), 95 g.  $(CF_3CO)_2O$  (VIII), and 400 ml.  $CCl_4$  stirred 4.5 hrs. at room temperature under N in a sealed flask wrapped in Al foil, the mixture poured into excess aqueous  $NaHCO_3$ , the aqueous layer extracted with  $CH_2Cl_2$ , the combined organic solutions washed with  $H_2O$ , 2N KOH, and  $H_2O$ , dried, and concentrated gave 7.90 g. 1,1'-( $\alpha$ -oxotrimethylene) ferrocene (IX), m. 146-7° (hexane). Several repetitions of the above reaction gave 68-87 percent IX. In 1 run the mother liquor from crystallization was concentrated to small volume and

chromatographed on  $\text{Al}_2\text{O}_3$  to give 4 percent  $\beta$ -ferrocenyl-ethyl trifluoromethyl ketone, m.  $34.5-5.0^\circ$ ,  $\nu$  1760, 1110, and 1103  $\text{cm}^{-1}$ . VI (2.6 g.) treated 16 hrs. at  $5^\circ$  with 75 ml. VIII (no  $\text{CCl}_4$  used), the mixture extracted with 3 75-ml. portions  $\text{Et}_2\text{O}$ , the combined extracts washed with excess saturated aqueous  $\text{NaHCO}_3$  and  $\text{H}_2\text{O}$ , dried evaporated, the residual product chromatographed on acid-washed  $\text{Al}_2\text{O}_3$ , eluted with  $\text{C}_6\text{H}_6$ , and the combined ketonic fractions concentrated gave 0.73 g. IX, m.  $145.5-6.5^\circ$  (pentane). VI (2.6 g.) and 25 ml. cold  $\text{PCl}_3$  stirred overnight at room temperature, the excess  $\text{PCl}_3$  removed in vacuo ( $\text{H}_2\text{O}$  pump), the residual crude acid chloride ( $\nu$  1790 and 1705  $\text{cm}^{-1}$ ) dissolved in  $\text{CH}_2\text{Cl}_2$ , the solution added dropwise to 1.5 g. anhydrous  $\text{AlCl}_3$  and 100 ml.  $\text{CH}_2\text{Cl}_2$  with cooling and stirring the mixture kept overnight at room temperature, poured over ice, the aqueous phase extracted repeatedly with  $\text{CH}_2\text{Cl}_2$ , the combined organic solutions washed with  $\text{H}_2\text{O}$  and saturated aqueous  $\text{Na}_2\text{SO}_4$ , filtered, the filtrate chromatographed on acid-washed  $\text{Al}_2\text{O}_3$ , the chromatogram developed with  $\text{C}_6\text{H}_6$ , and eluted with 2:1  $\text{CH}_2\text{Cl}_2$ -pentane gave (from an orange band) 0.8 g. IX, m.  $145^\circ$ ; the aqueous phase from the original Friedel-Crafts reaction made strongly acid with concentrated  $\text{HCl}$ , treated with 50 g.  $\text{SnCl}_2$ , the product isolated with  $\text{Et}_2\text{O}$ , and crystallized from cyclohexane gave 0.1 g. VI. Finely powdered VI (2.6 g.) and 60 g. Ia kept 43 hrs. at room temperature with occasional stirring, the mixture poured over ice, extracted with  $\text{Et}_2\text{O}$ , the combined extracts washed with  $\text{H}_2\text{O}$ , saturated aqueous  $\text{NaHCO}_3$ , and  $\text{H}_2\text{O}$ , dried, concentrated, chromatographed on acid-washed  $\text{Al}_2\text{O}_3$ , and the column eluted with 2:1  $\text{CH}_2\text{Cl}_2$ -pentane gave 0.40 g. IX, m.  $145-5^\circ$ ; acidification of the aqueous  $\text{NaHCO}_3$  wash gave 37.5 mg. VI, m.  $113^\circ$ . IX (2.0 g.) in 150 ml. anhydrous  $\text{Et}_2\text{O}$  added during 30 min. to 160 ml. approximately N  $\text{Et}_2\text{O-LiAlH}_4$  the mixture stirred 45 min. at room temperature, the excess  $\text{LiAlH}_4$  decomposed by slow addition of  $\text{EtOAc}$ , the mixture poured into ice-dilute  $\text{HCl}$ , the organic layer separated, washed with  $\text{H}_2\text{O}$ , dried, concentrated, and the residue treated with pentane gave 1.27 g. 1,1'-( $\alpha$ -hydroxytrimethylene)ferrocene (X), m.  $159^\circ$  (pentane). X (400 mg.), 2.5 g.  $\text{Al}_2\text{O}_3$ , and 12 ml. dry  $\text{C}_6\text{H}_6$  stirred 30 min. under N, the  $\text{Al}_2\text{O}_3$  filtered off, washed repeatedly with  $\text{Et}_2\text{O}$ , the combined organic solutions evaporated, and the residual solid chromatographed on  $\text{Al}_2\text{O}_3$  gave no olefin formed from a dehydration of X; elution with 1 percent  $\text{Et}_2\text{O}$  in hexane gave 37 mg.  $\alpha$ ,  $\alpha'$ -bis-trimethyleneferrocenyl ether (the diether formed from 2 molecules (X), m.  $220-3^\circ$  (decomposition)

(C<sub>6</sub>H<sub>6</sub>-hexane); elution with 20 percent Et<sub>2</sub>O in hexane gave 0.340 g. unchanged X. Treatment of X with pyridine-POCl<sub>3</sub> at 0° gave only unchanged X. AlCl<sub>3</sub> (6.0 g) in 60 ml. dry Et<sub>2</sub>O added dropwise to 1.14 g. LiAlH<sub>4</sub> slurried in 50 ml. Et<sub>2</sub>O under N with stirring, the mixture stirred 15 min. at room temperature, treated with 7.6 g. IX in 350 ml. dry Et<sub>2</sub>O, refluxed 3.5 hrs., cooled in an ice bath, the excess reagent decomposed with wet Et<sub>2</sub>O and then H<sub>2</sub>O, the aqueous layer separated, extracted with Et<sub>2</sub>O, the combined Et<sub>2</sub>O solutions dried, and concentrated gave 7.1 g. 1,1'-trimethylene-ferrocene, m. 107.5-8.0° (petr. ether). Zn dust (200 g.) 25 g. HgCl<sub>2</sub>, 10 ml. concentrated HCl, and 250 ml. H<sub>2</sub>O shaken 10 min., the Zn amalgam filtered off, washed with 3 percent HCl, mixed with 230 ml. H<sub>2</sub>O, 230 ml. concentrated HCl, 230 ml. C<sub>6</sub>H<sub>6</sub>, and 43 g. β-ferrocenoylpropionic acid in 230 ml. MeOH, the mixture refluxed overnight, the organic layer washed with 4 100-ml. portions H<sub>2</sub>O, dried, concentrated to 30 ml. chromatographed on Al<sub>2</sub>O<sub>3</sub>, the column eluted with C<sub>6</sub>H<sub>6</sub>, the eluate evaporated, the residue heated 30 min. on a steam bath with 60 ml. 10N NaOH, and the solution acidified to pH 2 with H<sub>3</sub>PO<sub>4</sub> gave 36 g. γ-ferrocenyl-butyric acid (XI), m. 115-16°. XI (9.84 g.) dissolved in 40 g. precooled (-70°) VIII, the solution stirred 75 min. at 0°, poured over ice, extracted repeatedly with Et<sub>2</sub>O, the combined extracts washed with H<sub>2</sub>O, aqueous Na<sub>2</sub>CO<sub>3</sub>, and H<sub>2</sub>O, dried, concentrated, the residual oil chromatographed on Al<sub>2</sub>O<sub>3</sub>, and the column eluted with C<sub>6</sub>H<sub>6</sub>-Et<sub>2</sub>O gave 7.88 g. 1,2-(α-oxo-tetramethylene) ferrocene (XII), m. 87.5-8.5° (Et<sub>2</sub>O). XI (0.5 g.) and Ia kept 4 hrs. at room temperature with occasional stirring, the solution poured over ice, extracted with Et<sub>2</sub>O, the extract washed with aqueous Na<sub>2</sub>CO<sub>3</sub>, the alkaline washed extracted with Et<sub>2</sub>O, the combined Et<sub>2</sub>O solutions dried, concentrated on a steam bath, chromatographed, and the product eluted with C<sub>6</sub>H<sub>6</sub> gave 75 mg. XII, m. 84.0-4.5°. Di-Et 1,1'-ferrocene bis (α-oxobutyrate) (m. 135-6°) (4.0 g.) in 30 ml. C<sub>6</sub>H<sub>6</sub> refluxed 4 hrs. with 20 g. amalgamated Zn, 15 ml. HCl, and 15 ml. H<sub>2</sub>O the C<sub>6</sub>H<sub>6</sub> layer separated, washed with H<sub>2</sub>O, aqueous NaHCO<sub>3</sub>, and aqueous Na<sub>2</sub>SO<sub>4</sub>, the aqueous layer extracted twice with C<sub>6</sub>H<sub>6</sub>, the combined extracts washed, dried, the combined C<sub>6</sub>H<sub>6</sub> solutions concentrated, chromatographed on Al<sub>2</sub>O<sub>3</sub> with C<sub>6</sub>H<sub>6</sub>, the center part of a broad ester band evaporated, the residue sapond. by heating with NaOH in EtOH, the solution diluted with H<sub>2</sub>O, extracted with Et<sub>2</sub>O, acidified with H<sub>3</sub>PO<sub>4</sub>, extracted with Et<sub>2</sub>O, the extract washed with H<sub>2</sub>O, dried and the Et<sub>2</sub>O displaced with hexane

gave 0.45 g. ferrocene 1,1'-butyric acid (XIII), m. 109-10°. XIII (0.45 g.) added to 5.0 g. VIII at -70°, the mixture swirled 30 min. in an ice bath, allowed to reach room temperature during 1 hr., poured over ice-NaOH, extracted with Et<sub>2</sub>O, the extract washed, dried, filtered, the filtrate chromatographed on Al<sub>2</sub>O<sub>3</sub>, and eluted first with 5 percent Me<sub>2</sub>CO in Et<sub>2</sub>O (5.6 mg. XII, present as an impurity in the starting XIII, was removed) and then 20 percent Me<sub>2</sub>CO in Et<sub>2</sub>O gave 0.176 g. mixture (XIV) of isomeric diketones (XV and XVI). Recrystallization of XIV from Et<sub>2</sub>O-Me<sub>2</sub>CO and the resulting product [31.6 mg., m. 153-61° (decomposition)] recrystallized twice from Et<sub>2</sub>O-Me<sub>2</sub>CO gave 1 isomer m. 167-8°: the



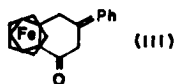
mother liquor from the first recrystallization concentrated, the Me<sub>2</sub>CO-Et<sub>2</sub>O displaced by hexane, the solution cooled to -70°, and the product (104.6 mg., m. 134.0-5.5°) repeatedly recrystallized from hexane gave 69.4 mg. other isomer, m. 135.0-5.5°. δ-Ferrocenylylalic acid (XVII) (500 mg.) and Ia kept 4 hrs. with occasional stirring, poured over ice, extracted with Et<sub>2</sub>O, the extract washed with aqueous Na<sub>2</sub>CO<sub>3</sub> and H<sub>2</sub>O, dried, concentrated to a small volume, chromatographed on Al<sub>2</sub>O<sub>3</sub>, and the column eluted with C<sub>6</sub>H<sub>6</sub> gave 70 mg. 1,2-(α-oxopentamethylene) ferrocene (XVIII), m. 61-3°. XVII (0.30 g.) added slowly to 10 ml. VIII, the mixture cooled to 5°, kept 16 hrs. with occasional shaking, poured over ice, and worked up as above gave 80 mg. XVIII, m. 57-8°. ε-Ferrocenylaproic acid (XIX) (1.09 g.) and 21 g. Ia kept 10 hrs. at room temperature and 4 hrs. at 56° with occasional stirring, cooled, poured over ice, extracted with Et<sub>2</sub>O and then CH<sub>2</sub>Cl<sub>2</sub>, an undissolved precipitate in the aqueous layer filtered off, washed with H<sub>2</sub>O, digested with Me<sub>2</sub>CO, and dried in vacuo gave 0.12 g. intermolecular condensation product, decompose about 200°; the Et<sub>2</sub>O and CH<sub>2</sub>Cl<sub>2</sub> extracts each washed with H<sub>2</sub>O, aqueous Na<sub>2</sub>CO<sub>3</sub>, and H<sub>2</sub>O, dried, evaporated, and chromatographed on Al<sub>2</sub>O<sub>3</sub> gave (from the Et<sub>2</sub>O extract) 2 small neutral chromatographic bands and (from the CH<sub>2</sub>Cl<sub>2</sub> extract) chiefly recovered XIX and only very little neutral material. Infrared and ultraviolet spectral data were given.

4. Schlogel, K., Mohar, A., and Peterlik, M.,  
PREPARATION OF ALKYL FERROCENES FROM ACYL-  
FERROCENES BY REDUCTION WITH LITHIUM-ALUMINUM  
HYDRIDE-ALUMINUM CHLORIDE, (Foreign Title Not Available),  
Translated into English from the German by U. S. Army  
Missile Command, Redstone Arsenal, Alabama, RSIC-536  
(Montashefte fuer Chemie, Vol. 92, 1961, pp. 921-926).

Refer to item No. 149 for abstract.

375. Tirouflet, J., Dabard, R., and Gautheron, B.,  
EXO AND ENDO ISOMERS IN THE FERROCENE SERIES.  
ACTION OF FERROCENE ON SUBSTITUTED SUCCINIC  
ANHYDRIDES, Comptes Rendus, Vol. 256, No. 6, 1963,  
pp. 1315-1316.

Condensation in the presence of  $\text{AlCl}_3$  of ferrocene with  $\alpha$ -phenyl- and  $\alpha$ -methylsuccinic anhydrides leads, in each case, to 2 oxo acids,  $\text{FcCOCH}_2\text{CHRCO}_2\text{H}$  (I) and  $\text{FcCOCHRCH}_2\text{CO}_2\text{H}$  (II), where Fc = ferrocenyl. These acids can readily be lactonized by dehydration in their enolic form. Clemmensen reduction and cyclization with polyphosphoric acid of II R = Ph,  $172^\circ$  (Me ester m.  $150^\circ$ ), yielded only 1,2-ferrocene-5-phenyl-3-cyclohexanone (III), m.  $148^\circ$ . In contrast, I (R = Ph), m.  $190^\circ$  (Me ester m.  $109^\circ$ ), gave 2 stereoisomeric 1,2-ferroceno-4-phenyl-3-cyclohexanones, m.  $154^\circ$  (exo), and  $184^\circ$  (endo). This is the first known example of endo-exo crystalline isomers in the sandwich series of molecules. The following products and intermediates were also prepared. I (R = Me) (m.  $145^\circ$ ), II (R = Me), (m.  $156^\circ$ ), 4-ferrocenyl-2-phenyl-3-buten-1,4-olide (m.  $164^\circ$ ), 4-ferrocenyl-3-phenyl-3-buten-1,4-olide (m.  $139^\circ$ ),  $\gamma$ -ferrocenyl- $\alpha$ -phenylbutyric acid (m.  $131^\circ$ ; Me ester m.  $75^\circ$ ), and  $\gamma$ -ferrocenyl  $\beta$ -phenylbutyric acid (m.  $118^\circ$ ; Me ester m.  $51^\circ$ ).

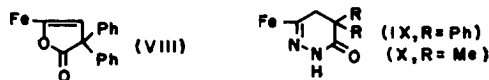


376. Tirouflet, J., Gautheron, B., and Dabard, R.,  
METALLOCENES. V. CONDENSATION OF FERROCENE WITH  
ANHYDRIDES OF DIBASIC ACIDS AND ORIENTATION OF THE  
REACTION IN THE CASE OF UNSYMMETRIC COMPOUNDS.  
Société Chimique de France, Bulletin, No. 1, 1965, pp. 96-  
102 (In French) (cf. CA 61, 684f).

A solution of 112 g. ferrocene in 400 ml.  $\text{CH}_2\text{Cl}_2$  was added slowly with vigorous shaking to a suspension of 52 g.  $\alpha$ -methylsuccinic anhydride, and 80 g.  $\text{AlCl}_3$  in  $\text{CH}_2\text{Cl}_2$ . Shaking was continued for a further 2 hrs. at room temperature and the mixture poured onto 250 g. ice and 16 ml concentrated  $\text{HCl}$  to give 87 g. of a mixture of 60 percent  $\text{FcCO-CH}_2\text{CHMeCO}_2\text{H}$  (I) and 40 percent  $\text{FcCOCHMeCH}_2\text{CO}_2\text{H}$  (II) (Fc = ferrocenyl). The pure products were separated by extraction of the crude material with  $\text{Et}_2\text{O}$  and filtering. Petr. ether (b.  $50-60^\circ$ ) was then added to the filtrate and the solution set aside to slowly evaporate. The resultant crystals were hand separated to give orange I, m.  $144^\circ$ , and orange-red II, m.  $156^\circ$ . Apart from using a N atm. during the addition of FcH, essentially the same conditions and molar amounts were used to synthesize 70 percent  $\text{FcCOCH}_2\text{CHPhCO}_2\text{H}$  (III) (m.  $190^\circ$ ) and 30 percent  $\text{FcCOCHPhCH}_2\text{CO}_2\text{H}$  (IV) (m.  $164^\circ$ ) from FcH and  $\alpha$ -phenylsuccinic anhydride. The crude product mixture formed as a red oil and the 2 components were separated by chromatography using an alumina column and  $\text{C}_6\text{H}_6$  as solvent and eluting agent. The first fraction contained unreacted FcH, then followed IV, and finally III. The Me esters of acids I-IV were synthesized by reaction with  $\text{CH}_2-\text{N}_2$  in  $\text{Et}_2\text{O}$ ; m.ps. were 58, 62, 110, and  $150^\circ$ , respectively. I was directly synthesized by reaction of  $\text{FcCOCH:CHMe}$  (m.  $110^\circ$ ) (from FcH and  $\text{CH}_3\text{CHClCH}_2\text{COCl}$  in the presence of  $\text{AlCl}_3$  under conditions similar to the synthesis of I-II mixtures) in  $\text{EtOH}$  with aqueous KCN to form  $\text{FcCOCH}_2\text{CHMeCN}$  (V), m.  $86^\circ$  (hexane). V (4.6 g.) gave 3 g. I when refluxed 5 hrs. with 35 ml.  $\text{EtOH}$  and 7 g. KOH dissolved in 110 ml.  $\text{H}_2\text{O}$ . Direct synthesis of III was effected by treating a mixture of 9.2 g. FcAc and 6 g.  $\text{PhCHBrCO}_2\text{H}$  with a solution of 6.3 g. K dissolved in 100 ml. tert-BuOH at reflux temperature for 7 hrs. under an inert atm. II and IV were directly prepared from  $\text{FcCOCH}_2\text{R}$  [R = Me gave II; R = Ph (m.  $130^\circ$ ) gave IV] and  $\text{ICH}_2\text{CO}_2\text{H}$  in the presence of tert-BuOK but only in low yields. An alternative method utilizes  $\text{FcCOCH}_2\text{R}$  in a Mannich reaction to give  $\text{FcCOCHRCH}_2\text{NMe}_2$  (m.  $68^\circ$  for R = Me), and treatment of these bases with MeI gives the quaternary



ammonium salts  $\text{FcCOCHRCH}_2\text{NMe}_3\text{I}$  [m.  $230^\circ$  (decomposition), for  $\text{R} = \text{Me}$  and  $\text{Ph}$ ]. These salts react with aqueous KCN to give  $\text{FcCOCRCH}_2\text{CN}$  (m.  $78-80^\circ$ ,  $\text{R} = \text{Me}$ ; m.  $126^\circ$ ,  $\text{R} = \text{Ph}$ ) and these in turn are hydrolyzed to II and IV with aqueous alcohol KOH. With  $\alpha, \alpha$ -diphenylsuccinic anhydride and  $\text{FcH}$ , using conditions similar to the synthesis of I-II mixtures, only orange-red  $\text{FcCOCH}_2\text{CPh}_2\text{CO}_2\text{H}$  (VI), m.  $226^\circ$  (decomposition) (Me ester m.  $201^\circ$ ), was formed and similarly with  $\alpha, \alpha$ -dimethylsuccinic anhydride, the only product was orange  $\text{FcCOCH}_2\text{CMe}_2\text{CO}_2\text{H}$  (VII), m.  $206^\circ$ ; Me ester m.  $76^\circ$ . VI readily formed an ethylenic lactone (VIII) (m.  $146-7^\circ$ ) on

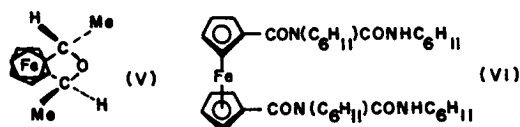


refluxing in  $\text{CH}_2\text{Cl}_2$  with trifluoroacetic anhydride under N for 6 hrs. and the reaction is reversed on addition of KOH. VI and VII both form pyridazinones [(IX), m.  $256^\circ$ , and (X), m.  $202-3^\circ$ , respectively] on heating their aqueous solutions with hydrazine hydrate.

377. Yamakawa, K., Ochi, H., and Arakawa, K.,  
ORGANOMETALLIC COMPOUNDS. I. TRANSFORMATION  
REACTIONS OF 1,1'-DIACETYLFERROCENE, Chem. Pharm.  
Bull. (Tokyo), Vol. 11, No. 7, 1963, pp. 905-911.

Oxidation of 7 g.  $\text{Fe}(\text{C}_5\text{H}_4\text{Ac})_2$  (I) in aqueous MeOH with NaOCl solution at  $5^\circ$  for 30 min. (temperature raised to  $50^\circ$  during an additional 35 min.) and acidification of the Na salt produced gave 6.2 g. orange-red  $\text{Fe}(\text{C}_5\text{H}_4\text{CO}_2\text{H})_2$  (II), m.  $240^\circ$  (decomposition) (AcOEt),  $\text{pK}$  6.8 (50 percent MeOH),  $\nu_{\text{KBr}}$  1690 ( $\text{CO}_2\text{H}$ ) and 1403  $\text{cm}^{-1}$ ,  $\lambda$  255 and 445  $\text{m}\mu$  ( $\epsilon$  9900 and 300, respectively). II esterified at  $0^\circ$  with saturated MeOH-HCl gave  $\text{C}_5\text{H}_4(\text{CO}_2\text{H})\text{FeC}_5\text{H}_4\text{CO}_2\text{Me}$  (37 percent), m.  $147-8^\circ$   $\text{C}_6\text{H}_6$ -petr. ether), and II refluxed with saturated MeOH-HCl for 2 hrs. yielded 82 percent  $\text{Fe}(\text{C}_5\text{H}_4\text{CO}_2\text{Me})_2$  (III), m.  $112-15^\circ$ ,  $\nu_{\text{KBr}}$  1704  $\text{cm}^{-1}$  ( $\text{CO}_2\text{Me}$ ). III polymerized with  $\text{HOCH}_2\text{CH}_2\text{OH}$  to give an insoluble orange-brown polymer. The oxidation of 10 g. I with 35 ml.  $\text{C}_5\text{H}_5\text{N}$  containing 11 g. iodine at room temperature for 8 hrs. produced 3.3 g.  $\text{C}_5\text{H}_4\text{AcFeC}_5\text{H}_4\text{CO}_2\text{H}$ , m.  $155-6^\circ$ ,  $\nu_{\text{KBr}}$  1725 ( $\text{CO}_2\text{H}$ ) and 1637  $\text{cm}^{-1}$  (Ac); Me ester m.  $91-4^\circ$  ( $\text{Et}_2\text{O}$ ). I reduced with  $\text{LiAlH}_4$  in tetrahydrofuran, and the reaction mixture decomposed with AcOEt

yielded  $\text{Fe}(\text{C}_5\text{H}_4\text{CHMeOH})_2$  (IV), m.  $69-71^\circ$  (Graham, et al., CA 51, 16440h), while the  $\text{LiAlH}_4$  reduction of I in  $\text{Et}_2\text{O}$ , and decomposition of the reaction mixture with dilute  $\text{HCl}$  produced the cyclic ether V, m.  $98-101^\circ$ , (Mashburn and Hauser, CA 55, 24707e). V was formed by treating IV with  $\text{Ac}_2\text{O}-\text{C}_5\text{H}_5\text{N}$  at room temperature, and in 98 percent yield by refluxing IV in  $\text{C}_6\text{H}_6$  containing an equal weight of  $p\text{-MeC}_6\text{H}_4\text{SO}_2\text{Cl}$ . It was postulated that IV,  $\nu_{\text{CS}_2} 3310 \text{ cm.}^{-1}$  (OH hydrogen bonded to Fe), had a  $\psi$ -endo configuration, and hence that V was the trans isomer. II (0.2 g.) in 60 ml.



anhydrous  $\text{Me}_2\text{CO}$  treated with 0.25 g.  $\text{C}_6\text{H}_{11}\text{N:C:NC}_6\text{H}_{11}$  for 8 hrs. at room temperature produced 0.19 g. VI, m.  $203-5^\circ$  (resolidified), and not the anhydride.

378. Zakharkin, L. I., Gavrilenko, V. V., and Maslin, D. N., PREPARATION OF ALDEHYDES BY REDUCTION OF ESTERS OF CARBOXYLIC ACIDS WITH SODIUM ALUMINUM HYDRIDE, Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 5, 1964, pp. 926-928.

Reduction of esters of carboxylic acids with  $\text{NaLiH}_4$  in tetrahydrofuran at  $-50^\circ$  gave in 1 hr. 45-88 percent corresponding aldehydes; the following were reduced to appropriate aldehydes: Me butyrate, Me caproate, Et  $\alpha, \alpha, \omega$ -trichlorocaproate, Et nicotinoate, EtOBz, Me *o*-chlorobenzoate, di-Me phthalate, Me cinnamate, Me hydrocinnamate, di-Me sebacate, Et undecylenate, Et laurate, Me oleate, Et  $\delta$ -cyanovaleate, Me ferrocenecarboxylate,  $\delta$ -valerolactone, and tridecanolide. The yields dropped sharply at lower or higher temperatures. At higher temperatures the reduction to alcohols appeared.

#### D. Nitrogen Containing Ferrocene Derivatives

379. Berry, R. A., Jr.,  
PART I: A STUDY OF THE HUNSDIECKER REACTION.  
PART II: THE BASICITIES OF THE FERROCENYLAZOBENZENES, University Microfilms (Ann Arbor, Michigan),  
Order No. 63-3478, Dissertation Abstract, Vol. 23, 1963,  
pp. 4529-4530.

The Hunsdiecker reaction on the silver, mercury (II), and lead (II) salts of the straight chain carboxylic acids, valeric through capric acids with the exception of nonanoic acid, was studied. The branched chain acids, iso-caproic,  $\alpha$ -ethyl-n-caproic, and iso-butyric acids, were subjected to the reaction. The mercury and lead salts were found to react more sluggishly than their corresponding silver salts. However, the mercury salts were found to be just as effective as the silver salts in degrading carboxylic acids to alkyl bromides of one less carbon atom.

Attempts to carry out the Hunsdiecker reaction on 6-nitro-2'-carbomethoxybiphenyl-2-carboxylic acid gave unidentifiable products. Treatment of the silver and mercury salts of 4, 6, 4', 6'-tetranitro-2,2'-diphenic acid with bromine gave only recovery of the parent acid.

The pK values of several substituted ferrocenylazobenzenes were measured in 20 volume percent ethanol-80 volume percent aqueous sulfuric acid. In each case the substituted m- and p-ferrocenylazobenzenes were found to be weaker bases than their corresponding monosubstituted azobenzenes. The electron withdrawing property of the ferrocenyl group in the ferrocenylazobenzenes is in direct contrast to the electron donating character usually exhibited by the ferrocenyl group; the ferrocenylanilines are stronger bases than aniline itself while ferrocenylphenol is a weaker acid than phenol, and the ferrocenylbenzoic acids are weaker than benzoic acid.

This electron withdrawing property of the ferrocenyl group in the ferrocenylazobenzenes can best be explained by protonation of the iron in the ferrocenyl group by the highly acidic solvent in which the measurements were made. This protonation was demonstrated by extracting the free ferrocenylazobenzene base with carbon tetrachloride from a 50 percent sulfuric acid solution of its conjugate acid which had been diluted and neutralized.

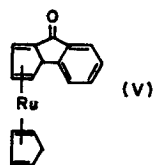
Hammett sigma constants were found for the m- and p-ferrocenyl groups by substituting the pK values obtained for the m- and p-ferrocenylazobenzenes into the Hammett equation of other monosubstituted azobenzenes. The pK values of the substituted ferrocenylazobenzenes gave a good Hammett equation correlation, especially when the p-ferrocenylazobenzenes and m-ferrocenylazobenzenes were treated as individual series. Sigma plus values were required for those substituents which could resonate with the reaction site (i. e., the basic center). Correlation of the results of these experiments with measurements of the pK values of disubstituted azobenzenes demonstrates that the p-ferrocenyl group itself does not resonate with the reaction site in ferrocenylazobenzenes; thus, the sigma value obtained for the p-ferrocenyl group is a normal sigma rather than a sigma plus.

380. Bublitz, D. E., McEwen, W. E., and Kleinberg, J., COMPARISON OF REACTIVITIES OF METALLOCENYL-PHENYLCARBINYL AZIDES IN ACID-CATALYZED DECOMPOSITION REACTIONS, American Chemical Society Journal, No. 84, 1962, pp. 1845-1849.

The metallocenylphenylcarbinyl azides derived from Fe, Ru, and Os give different sets of products with  $H_2SO_4$ . Benzoylruthenocene (I) (0.25 g.) was reduced in dry  $Et_2O$  with 0.13 g.  $LiAlH_4$  for 45 min. The mixture was poured into brine and the solution filtered and extracted with ligroine. The extract was dried ( $Na_2SO_4$ ) and evaporated to give 0.23 g. phenylruthenocenylcarbinol (II), m.  $105.6-6.2^\circ$  (ligroine). To 0.5 g. II was added 5 cc. 1.2N solution of  $HN_3$  in  $C_6H_6$  followed by 1 drop of  $HCO_2H$ . The mixture was left at room temperature for three days under N and the product chromatographed over  $Al_2O_3$  (activity III). Elution with  $C_6H_6$  gave 0.48 g. phenylruthenocenylcarbinylazide (III), as a yellow oil, crystallizing after three weeks, m.  $48.5-50^\circ$ ,  $n_D^{25}$  1.6432,  $d_{25.5}$  1.502. To a stirred mixture of 22.6 cc. dry  $CHCl_3$  and 13.6 cc. concentrated  $H_2SO_4$  was added 0.82 g. III and the reaction followed by measuring the N evolved (24 hrs.). The mixture was poured into ice and extracted with  $CHCl_3$ ; the extract was dried ( $MgSO_4$ ) and evaporated and the residue chromatographed  $Al_2O_3$ . Besides 0.028 g. eluted by ligroine, 0.043 g. ruthenocenecarboxaldehyde (IV), m.  $100.2-100.8^\circ$ , was eluted by 2 percent  $Et_2O$  in ligroine. Further elution gave orange V (2,3-ruthenocoindene), m.  $134.2-5^\circ$  (ligroine- $C_6H_6$ )  $\lambda$  253, 397 m $\mu$ . Semicarbazone of IV m.  $208.8.4^\circ$

(EtOH-H<sub>2</sub>O); 2,4-dinitrophenylhydrazone, m. 220-2°. In another run 2 g. III with 56 ml. CHCl<sub>3</sub> and 33 ml. H<sub>2</sub>SO<sub>4</sub> as above gave 50 mg. ruthenocene (VI) and 90 mg. V but no IV. PhNH<sub>2</sub> equivalent to IV was also isolated. To 1.84 g. III was added 50 ml. of 5M H<sub>2</sub>SO<sub>4</sub> in glacial HOAc, and the mixture stirred 48 hrs. at room temperature (N evolved, 0.142 g.). The mixture was poured on 200 g. ice, the solution was concentrated and extracted with C<sub>6</sub>H<sub>6</sub> continuously. The residue after removing C<sub>6</sub>H<sub>6</sub>, was chromatographed over Al<sub>2</sub>O<sub>3</sub>. Elution with ligroine gave 0.19 g. bis(phenylruthenocenylmethyl) ether (VII), m. 153.4-4.4°. Elution with 10 percent ether-ligroine mixture gave in the following order 0.07 g. I, 0.12 g. VII, and 0.22 g. II. III (1.8 g.) gave with 10M H<sub>2</sub>SO<sub>4</sub> in HOAc 0.65 g. VII, 0.05 g. V. To 1.63 g. POCl<sub>3</sub> and 1.35 g. N-methylformanilide which has been stirred for 90 min. was added 19 cc. PhCl and 1.66 g. VI and the mixture stirred at 90° for 2.5 hrs. and for 2 hrs. at room temperature. Saturated NaOAc solution was added during 15 min. and the aqueous solution extracted with C<sub>6</sub>H<sub>6</sub>. The extract was dried and evaporated and the residue chromatographed over Al<sub>2</sub>O<sub>3</sub>. VI (0.17 g.) was eluted first and then 0.17 g. IV. Heating 1 g. II with 1 g. Cu powder at 210° for 10 min. and extracting the mixture C<sub>6</sub>H<sub>6</sub> followed by chromatography on Al<sub>2</sub>O<sub>3</sub> gave 0.45 g. VII. o-Ferrocenylbenzoic acid (VIII) was prepared by the action of diazotized anthranilic acid on ferrocene. VIII was cyclized by treatment of the acid chloride with freshly sublimed AlCl<sub>3</sub> in CH<sub>2</sub>Cl<sub>2</sub> for 2 hrs. at room temperature to give 0.7 g. 2,3-ferrocoindenone (IX), dark purple, m. 105-6.2° (ligroine). Benzoylosmocene (X) (0.25 g.) was reduced with 0.1 g. LiAlH<sub>4</sub> for 0.5 hr. to give 0.23 g. osmocenyl phenylcarbinol (XI), m. 115.7-16° (ligroine). To 0.5 g. XI was added 5 ml. of 1.2N solution of HN<sub>3</sub> in C<sub>6</sub>H<sub>6</sub> followed by a drop of HCO<sub>2</sub>H and the mixture left at room temperature for three days. Evaporation and chromatography over Al<sub>2</sub>O<sub>3</sub> gave 0.47 g. osmocenylphenylcarbiny azide (XII),  $n_D^{23}$  1.6540,  $d_{27}$  1.892. XII (0.45 g.) in 5.2 cc. CHCl<sub>3</sub> was treated with 2.6 cc. 100 percent H<sub>2</sub>SO<sub>4</sub> at 0° and the mixture stirred at room temperature for 15 hrs. (N evolved, 50 percent). The mixture was poured on ice and extracted with CHCl<sub>3</sub>. The extract was dried (MgSO<sub>4</sub>), evaporated, and chromatographed over Al<sub>2</sub>SO<sub>3</sub> to give 0.28 g. X besides other uncharacterized products. The first order rate constants were determined for some of these reactions. During the preparation of X (Selin and West, CA 57, 8601h.) a new dibenzoylruthenocene, m. 141.8-2.4° was obtained by chromatography on Al<sub>2</sub>O<sub>3</sub> and

elution with 14 percent ether-ligroine. An explanation of the exclusive formation of X from XII based on the greater donor properties of Os is given.



381. Duke University, Durham, North Carolina,  
RING METALATION OF DIMETHYLAMINOMETHYL-  
FERROCENE WITH BUTYLLITHIUM AND CONDENSATIONS  
WITH ELECTROPHILIC COMPOUNDS. SYNTHESIS OF 1,2-  
DISUBSTITUTED FERROCENES by D. W., Slocum, B. W.  
Rockett, and C. R. Hauser, September 1964, Report No.  
AROD 3581 7, AD-614 544, Contract No. DA ARO D31 124G409  
(American Chemical Society Journal, Vol. 87, No. 6,  
20 March 1965, pp. 1241-1246) (Unclassified Report).

N, N-Dimethylaminomethylferrocene (I) was metalated with n-butyllithium in ether-hexane, and the resulting monolithioamine was condensed with benzophenone acetone, benzonitrile, and phenyl isocyanate to form the corresponding 2-derivatives. The methiodide (II) of the benzophenone adduct was cyclized by means of potassium amide to give the cyclic ether.

Methiodide II was also treated with potassium hydroxide and potassium cyanide to afford the diol and carbinol-nitrile, respectively. Amine I was metalated with excess N-butyl-lithium in THF-hexane and the resulting intermediates were condensed with benzophenone to yield mainly the 2, 1'-derivative; also, some of the 2- and the 1'-derivatives were formed. These results furnish a route to the synthesis of a number of new 1,2-disubstituted and 1,2,1'-trisubstituted ferrocenes. Amine I underwent lithiation more readily than ferrocene. In THF-hexane, amine I was converted primarily to a dilithio-amine. Some infrared and N. M. R. spectral correlations of 1,2-disubstituted ferrocenes are discussed.

82. Furdik, M., Toma, S., and Suchy, J.,  
DERIVATIVES OF FERROCENE. VII. DIELS-ALDER  
REACTION OF N-FERROCENYLMALEIMIDE WITH COM-  
POUNDS OF DIENE CHARACTER, Chemie Avesti, Vol. 17,  
1963, pp. 21-30 (cf. CA 59, 3955g).

Diels-Alder reaction of N-ferrocenylmaleimide (as the dienophile) with cyclopentadiene, dimethylfulvene, ferrocenylfulvene,  $\alpha$ -cyclopentadienylideneethylferrocene, furan, and  $\alpha$ -methylfuran was described. These previously unknown bicyclic adducts were prepared: N-ferrocenylbicyclo [1.2.2] hept-5-ene-2,3-dicarboximide, m. 184°; N-ferrocenyl-7-dimethylmethylenebicyclo [1.2.2] hept-5-ene-2,3-dicarboximide (I), m. 168-70°; N-ferrocenyl-1,4-endoxo-5-cyclohexene-2,3-dicarboximide, m. 155-7°; N-ferrocenyl-1-methyl-1,4-endoxo-5-cyclohexene-2,3-dicarboximide, m. 129-31°; N-ferrocenyl-7-ferrocenylmethylenebicyclo [1.2.2] hept-5-ene-2,3-dicarboximide, m. 192°; and N-ferrocenyl-7-methylferrocenylmethylenebicyclo [1.2.2] hept-5-ene-2,3-dicarboximide, m. 169-70°. All these compounds had the endo-isomeric configuration because the formation of the exo-isomeric configuration was sterically hindered by the ferrocenyl group bound on the imide N. The identity of all these adducts was also determined by infrared absorption spectra, showing wavelengths of 1110, 800-900, 1710-20, and 930  $\text{cm}^{-1}$ . The presence of the absorption maximum at 615-45  $\text{cm}^{-1}$  indicates the endo-isomeric form.

383. Hauser, C. R. and Lindsay, J. K.,  
ALKYLATIONS WITH THE MOTHODIDE OF N,N-  
DIMETHYLAMINOMETHYLFERROCENE. SYNTHESIS OF  
AN  $\alpha$ -AMINO ACID HAVING THE FERROCENE GROUP,  
Journal of Organic Chemistry, Vol. 22, 1957, pp. 1246-1247.

Refer to item No. 240 for abstract.

384. Nesmeyanov, A. N., Drozd, V. N., and Sazonova, V. A.,  
ACETYLATION OF N-ACYLAMINOFERROCENES, Izvestiya  
Akademii Nauk SSSR, Seriya Khimicheskaya, No. 7, 1965,  
pp. 1205-1208 (In Russian).

Heating N-ferrocenylphthalimide with  $\text{Ac}_2\text{O}$  in the presence  $\text{H}_3\text{PO}_4$  3 min. at 100° gave, after an aqueous treatment and chromatography on  $\text{Al}_2\text{O}_3$ , 40 percent 1'-N-phthalimido-1-acetylferrocene in two forms: red, m. 129.5-30.5°, and

bronze-yellow, m. 145.5-47°, the latter being the more stable one. The filtrate gave 7 percent homoannular N-phthalimidoacetylferrocene, m. 165.5-6.5°. Similar treatment of N-acetylferrocene gave 17 percent 1'-acetamido-1-acetylferrocene in two forms: yellow, m. 61-3°, and more stable red, m. 110-12°. 1'-Acetylferrocene-1-carboxylic acid in Me<sub>2</sub>CO was treated with Et<sub>3</sub>N, followed by MeO<sub>2</sub>CCl 20 min. at 0°, then by aqueous NaN<sub>3</sub>, and after 50 min. at 0° gave after an aqueous treatment 54.5 percent 1'-acetylferrocene-1-carboxazide, decomposed 122-3°, which heated under N atm. with PhCH<sub>2</sub>OH to 115-25° gave 85.5 percent 1'-carbobenzoxyamino-1-acetylferrocene, m. 128.5-9.5°, which refluxed with alcohol KOH under N 2 hrs. and acidified gave 81 percent 1'-amino-1-acetylferrocene, m. 95-6.5°, which with phthalic anhydride at 180° under N atm. gave 67 percent 1'-N-phthalimido analog, m. 145.5-47°. Keeping 1'-amino-1-acetylferrocene with Ac<sub>2</sub>O-pyridine 6 hrs. gave 85 percent 1'-acetamido-1-acetylferrocene, m. 61-3°, which heated 4 hrs. with alcohol KOH gave 74 percent 1'-amino-1-acetylferrocene, m. 94.596°, also obtained similarly from the 1-N-phthalimido analog.

385. Nesmeyanov, A. N., Nikitina, T. V., and Perevalova, E. G., CONDENSATION OF FERROCENYLAMINE WITH NITRO-SOBENZENE, Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 1, 1964, pp. 197-199.

Heating azoferrocene with Zn dust in EtOH-C<sub>6</sub>H<sub>6</sub> in the presence of concentrated HCl 15 min. (disappearance of violet color) gave after neutralization of the aqueous layer and extraction with Et<sub>2</sub>O, 100 percent ferrocenylamine, m. 151-4°, from combined organic layers. This and PhNO kept 6 hrs. in EtOH-AcOH gave 80 percent Fe<sub>2</sub>O<sub>3</sub> and 10 percent unreacted amine. Similar reaction in C<sub>6</sub>H<sub>6</sub> in the presence of 50 percent NaOH after heating 9 hrs. under N gave 23 percent unreacted amine and 56 percent benzeneazoferrocene (I), m. 109-10°, and 20 percent benzeneazoxyferrocene, m. 119-20°, the latter heated with Fe filings to 200° gave 65 percent I. Ultraviolet and mass spectra of the products were used to confirm their identities.



386. Nesmeyanov, A. N., Perevalova, E. G., Nikitina, T. V., and Kuznetsova, N. I.,

ACTION OF HYDROCHLORIC ACID ON AZO DERIVATIVES OF FERROCENE, Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 12, 1965, pp. 2124-2128 (In Russian).

Phenylazoferrocene and concentrated HCl in Et<sub>2</sub>O reacted with heat evolution and gave a yellow unidentified solid free of Fe and halogen; PhNH<sub>2</sub> was detected as was Fe hydroxide. m-Ferrocenylazobenzene similarly treated gave 25 percent unchanged material, 1.4 percent brown C<sub>22</sub>H<sub>20</sub>FeN<sub>2</sub>, decomposed 130-40° (evidently a derivative of ferrocenylhydrazobenzene), PhNH<sub>2</sub>, and m-ferrocenylaniline (48 percent), as well as Fe(OH)<sub>3</sub>. p-Ferrocenylazobenzene similarly treated gave 29 percent p-ferrocenylaniline, 24.7 percent starting material, and 2.1 percent violet C<sub>22</sub>H<sub>20</sub>FeN<sub>2</sub>, did not m. 200°, which was an isomerized product of ferrocenylhydrazobenzene.

387. Nesmeyanov, A. N., Perevalova, E. G., Nikitina, T. V., and Kuznetsova, N. I.,

BEHAVIOR OF M- AND P-FERROCENYLHYDRAZOBENZENES UNDER CONDITIONS OF THE BENZIDINE REARRANGEMENT, Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 12, 1965, pp. 2120-2124 (In Russian).

p-Ferrocenylaniline and PhNO<sub>2</sub> in AcOH-EtOH heated 10-15 min. gave a precipitate of p-ferrocenylazobenzene, 82 percent, m. 123-4°, augmented by working up the Et<sub>2</sub>O extract of the filtrate. Recrystallization from EtOH gave an orange form, m. 127-8°, and more solution darker orange form, m. 136-8°, which was more stable in storage, but which was convertible to the former by heating in hexane and cooling. Both had similar uv and ir spectra. Similarly was prepared, m-ferrocenylazobenzene, m. 109-11°. Reduction of the p-isomer with Zn dust in EtOH-C<sub>6</sub>H<sub>6</sub> and 20 percent NaOH gave in 30 min. p-ferrocenylhydrazobenzene, m. 162-2.5°, which oxidized during attempts at chromatographic purification on Al<sub>2</sub>O<sub>3</sub>. Similarly was obtained m-ferrocenylhydrazobenzene (I), m. 144-4.5°, which also was oxidized readily. I shaken with 1:1 aqueous HCl and Et<sub>2</sub>O at 30-40° gave 76 percent m-ferrocenylazobenzene and 6 percent brown C<sub>22</sub>H<sub>20</sub>FeN<sub>2</sub>, decomposed 135-40°, as well as some 60 percent PhHN<sub>2</sub> and m-ferrocenylaniline. Similar treatment of p-isomer of I gave 86 percent p-ferrocenylazobenzene, PhNH<sub>2</sub>, 74 percent p-ferrocenylaniline, and 3.5 percent violet solid, C<sub>22</sub>H<sub>20</sub>FeN<sub>2</sub>, did not m. 200°.

388. Nesmeyanov, A. N., Perevalova, E. G., and Yur'eva, L. P.,  
REACTION PRODUCTS OF CYANATION OF PHENYL-  
FERROCENE, Izvestiya Akademii Nauk SSSR, Seriya  
Khimicheskaya, No. 5, 1965, pp. 907-909 (In Russian).

The mixed nitriles of phenylferrocenecarboxylic acids reported earlier (Ca 55, 12378i) were converted to the amides which were separated on  $\text{Al}_2\text{O}_3$  into 39 percent 1-phenyl-2-carbamoylferrocene, m. 219-20°; 4 percent 1,3-isomer, m. 181-2°; 8 percent 1,1'-isomer, m. 127-8°; and 37 percent p-carbamoylphenylferrocene, m. 214-15°. The latter was also prepared from p-ferrocenylbenzoic acid by treatment with  $\text{SOCl}_2$ , and then by  $\text{NH}_4\text{OH}$ . The amide isomers were identified by ir spectra.

389. Nesmeyanov, A. N., Perevalova, E. G., Yur'eva, L. P., and Denisovich, L. I.,  
REACTION OF FERROCENECARBONITRILE WITH  
ORGANOMETALLIC COMPOUNDS AND THE PREPARATION  
OF DI-AND TRIFERROCENYLMETHYL COMPOUNDS,  
Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk,  
1962, pp. 2241-2243 (cf. CA 58, 7971b).

Refer to item No. 231 for abstract.

390. Nesmeyanov, A. N., Perevalova, E. G., Yur'eva, L. P., and Grandberg, K. I.,  
SYNTHESIS OF FERROCENE DERIVATIVES FROM NITRILES  
OF FERROCENECARBOXYLIC ACIDS, Izvestiya Akademii  
Nauk SSSR, Seriya Khimicheskaya, No. 8, 1963, pp. 1377-  
1380 (cf. CA 58, 7971h).

Refer to item No. 179 for abstract.

391. Nesmeyanov, A. N., Sazonova, V. A., Gerasimenko, A. V.,  
and Sazonova, N. S.,  
PHOTOLYSIS OF SALTS OF  $\alpha$ -PYRIDYLFERROCENE,  
Doklady Akademii Nauk SSSR, Vol. 149, No. 6, 1963, pp.  
1354-1355.

The combination of  $\alpha$ -pyridylferrocene and MeI in a mixture of EtOH-Et<sub>2</sub>O for several days formed a methiodide, a red solid. This substance, when irradiated with incandescent lamp light or sunlight, rapidly decomposed and gave 84 percent N-methyl-2-cyclopentadienylidene-1,2-dihydropyridine (I), m. 73-4.5°; some cyclopentadiene was also formed.

I gave a chloroplatinate, a solid (from  $\text{MeNO}_2\text{-Et}_2\text{O}$ ). Photolysis of the methiodide in aqueous oxalic acid gave Fe oxalate.

392. Nesmeyanov, A. N., Sazonova, V. A., and Romanenko, V. I., ALKYLATION OF FERROCENYLAMINE, Doklady Akademii Nauk SSSR, Vol. 152, No. 6, 1963, pp. 1358-1359.

Ferrocenylamine reacted exothermically with  $\text{Et}_3\text{O} \cdot \text{BF}_4$  (ice cooling) and after treatment with aqueous KOH and extraction with  $\text{Et}_2\text{O}$  gave 77 percent yellow ethylferrocenylamine (I), 1 m.  $56.5\text{-}8^\circ$ , which was sublimable in vacuo. After purification on  $\text{Al}_2\text{O}_3$ , the residue gave some diethylferrocenylamine (II), 1 m.  $35.5\text{-}6.5^\circ$ , formed by repetition of the above reaction in 95 percent yield. I.HCl, a solid, precipitated from  $\text{Et}_2\text{O}$  with dry HCl; II.HCl was a yellow unstable solid. I gave the p-tosyl derivative, m.  $105\text{-}5.5^\circ$ . II and EtI gave the ethiodide, yellow crystals (from  $\text{EtOH-Et}_2\text{O}$ ). All were unstable in aqueous acids in light.

393. Perevalova, E. G. and Ustynyuk, Y. A., REACTIVITY OF COMPOUNDS CONTAINING THE FERROCENYLMETHYL GROUP. III. REACTIONS OF QUATERNARY AMMONIUM SALTS CONTAINING THE FERROCENYLMETHYL RADICAL WITH ORGANOMAGNESIUM COMPOUNDS IN THE PRESENCE OF COBALT CHLORIDE, Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 10, October 1963, pp. 1776-1782 (cf. CA 59, 7557b).

$\text{PrMgCl}$  in  $\text{Et}_2\text{O}$  and dimethylbenzyl (ferrocenylmethyl)-ammonium chloride treated 4 hrs. at reflux with 25 mole-percent  $\text{CoCl}_2$  in tetrahydrofuran, refluxed 2 hrs. longer, poured on dry ice, then treated with aqueous  $\text{NH}_4\text{Cl}$  and HCl gave 10 percent  $(\text{PhCH}_2)_2$ , 64 percent N, N-dimethylamino-methylferrocene,  $b_3$   $110\text{-}12^\circ$ ,  $n_D^{20}$  1.5907 (methiodide decomposed  $208\text{-}12^\circ$ ), and 62 percent  $\text{PhCH}_2\text{CO}_2\text{H}$ , while the fore-run treated with MeI gave a little  $\text{PhCH}_2\text{NMe}_3\text{I}$ . Similarly,  $\text{EtMgBr}$  and dimethylbis (ferrocenylmethyl) ammonium bromide in the presence of  $\text{CoCl}_2$  gave 67 percent starting material, some methylferrocene and 1,2-diferrocenylethane.  $\text{EtMgBr}$  and dimethylpropyl (ferrocenylmethyl) ammonium bromide under similar conditions gave 73.5 percent starting salt, some unidentified red oil (which was devoid of N), and some crude propylferrocene.  $\text{EtMgBr}$  and dimethylallyl (ferrocenylmethyl) ammonium bromide (I) kept in  $\text{Et}_2\text{O}$  4 hrs. at room temperature, then quenched in ice- $\text{NH}_4\text{Cl}$ , gave 43

percent unreacted salt and 38 percent N, N-dimethylamino-methylferrocene; its yield rose to 86 percent when the reaction was extended to 7 hrs. The same reaction in the presence of  $\text{CoCl}_2$  (4 hrs. at reflux) gave 83 percent yield of the same amine.  $\text{MgBr}_2 \cdot \text{Et}_2\text{O}$ , prepared in situ from Mg and  $\text{BrCH}_2\text{CH}_2\text{Br}$ , was treated with dimethylallyl (ferrocenylmethyl) ammonium bromide which dissolved in the oily etherate layer (addition of tetrahydrofuran to this solution resulted in much heat evolution): the solution after 2 hrs. at room temperature was quenched in ice- $\text{NH}_4\text{Cl}$  to give 85 percent original salt. Since  $\text{CoCl}_2$  failed to affect the reaction of I with  $\text{RMgX}$ , it is suggested that this reaction was heterolytic rather than homolytic. The results indicated that the ferrocene nucleus stabilized the adjacent radical-forming centers to a lesser degree than did the Ph nucleus.

394. Perevalova, E. G., Ustynyuk, Y. A., and Nesmeyanov, A. N., REACTIVITY OF COMPOUNDS CONTAINING THE FERROCENYLMETHYL GROUP, COMMUNICATION 2. EMDE SODIUM AMALGAM REDUCTION OF QUATERNARY AMMONIUM SALTS CONTAINING THE FERROCENYLMETHYL GROUP, Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, No. 6, June 1963, pp. 1045-1049.

Refer to item No. 53 for abstract.

395. Perevalova, E. G., Ustynyuk, Y. A., and Nesmeyanov, A. N., REACTIVITY OF COMPOUNDS CONTAINING THE FERROCENYLMETHYL GROUP. I. HYDROLYTIC CLEAVAGE OF THE QUATERNARY AMMONIUM SALTS. II. EMDE REDUCTION BY NA AMALGAM OF QUATERNARY AMMONIUM SALTS CONTAINING THE FERROCENYLMETHYL RADICAL, Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, No. 6, 1963, pp. 1036-1049.

#### PART I

The following ferrocenylmethyl quaternary ammonium salts  $[\text{C}_5\text{H}_5\text{FeC}_5\text{H}_4\text{CH}_2\text{N}^+\text{Me}_2\text{CH}_2\text{R}]\text{X}^-$ , were prepared by the reaction of 4.86 g.  $\text{C}_5\text{H}_5\text{FeC}_5\text{H}_4\text{CH}_2\text{NMe}_2$  (I) in 5 ml. dry MeCN with a solution of 0.03M halide,  $\text{RCH}_2\text{X}$  (R, X, percent yield given): nonyl, Br, 78; nonyl, I, 94; Bu, I, 92; Pr, Br, 100; Et, I, 96;  $\text{CH}_2\text{CH}:\text{CH}_2$ , Br (II), 100;  $\text{CH}_2\text{Ph}$ , Cl (III), 100;  $\text{CH}_2\text{CO}_2\text{Et}$ , Cl (IV), 84;  $\text{CH}_2\text{Bz}$ , Br (V), 82; Pr, I, 88; Et, 2, 4, 6- $(\text{O}_2\text{N})_3\text{C}_6\text{H}_2\text{O}$ , 100; Me, 2, 4, 6- $(\text{O}_2\text{N})_3\text{C}_6\text{H}_2\text{O}$ , 100;  $\text{CH}_2\text{CH}:\text{CH}_2$ , I (VI), 89;  $\text{CH}_2\text{CH}:\text{CH}_2$ , 2, 4, 6- $(\text{O}_2\text{N})_3\text{C}_6\text{H}_2\text{O}$ , 100;  $\text{CH}_2\text{Ph}$ , I (VII), 100.  $[(\text{C}_5\text{H}_5\text{FeC}_5\text{H}_4\text{CH}_2)_2\text{N}^+\text{Me}_2]\text{Br}^-$

(VIII) was prepared in 83 percent yield from a mixture of 4.8 g. I, 5 ml. MeCN, and 7.4 g. iso-PrBr boiled 4 hrs. In the presence of aqueous NaOH,  $C_5H_5FeC_5H_4CH_2OH$  (IX) was obtained in 9.3-13.7 percent yield from  $[C_5H_5FeC_5H_4CH_2N^+Me_3]I^-$  (X), in 38.6 percent yield from  $[C_5H_5FeC_5H_4CH_2N^+Me_2CH_2CH:CH_2]Cl^-$ , in 23.1-37 percent yield from II, in 37 percent yield from VI, in 32.4-62.5 percent yield from III, in 64.8 percent yield from VII, in 37-82.2 percent yield from IV, and in 46.8 percent yield from VIII. Owing to the electrophilic catalysis of the acid formed, the yields of IX in these  $S_N1$  reactions were higher in  $H_2O$  than in aqueous NaOH: 13.7 percent from X, 55.5 percent from II, 69.7 percent from III, 89 percent from IV, and 74-89.5 percent from V. The rate of hydrolysis increased as the electrophilicity and length of the C-chain of the  $RCH_2$  group increased. As was expected for an  $S_N1$  mechanism, hydrolysis of VII with NaOH in 50 percent  $H_2O$ -dioxane in which the I formed was soluble gave lower yields of IX than hydrolysis in aqueous NaOH. 29 references.

## PART II

In quaternary ferrocenylmethylammonium salts, the stabilizing action of groups on the adjacent radical increased in the order: Me,  $CH_2:CHCH_2$ ,  $C_5H_5FeC_5H_4CH_2$ ,  $PhCH_2$ . Thus, from the  $Et_2O$  extract of a reaction mixture of 3.85 g.  $[C_5H_5FeC_5H_4CH_2N^+Me_3]I^-$ , 150 ml.  $H_2O$ , and a Na amalgam containing 20 g. Na and 20 ml. Hg, 89 percent  $C_5H_5FeC_5H_4Me$  (I) < 1 percent  $C_5H_5FeC_5H_4CH_2NMe_2$  (II), and a small amount of  $(C_5H_5FeC_5H_4CH_2)_2O$  (III) were separated. Similar reduction of  $[C_5H_5FeC_5H_4CH_2N^+Me_2CH_2CH:CH_2]Br^-$  or  $[C_5H_5FeC_5H_4CH_2N^+Me_2CH_2Ph]Cl^-$  gave 30 percent I, 7.8 percent III, 4.6 percent  $C_5H_5FeC_5H_4CH_2OH$ , and 26.2 percent II, or 64 percent II, 19 percent I, and a small amount of III, respectively.

396. Perevalova, E. G., Ustynyuk, Y. A., Ustynyuk, L. A., and Nesmeyanov, A. N.,  
 REACTIVITY OF COMPOUNDS CONTAINING THE FERROCENYLMETHYL GROUP, COMMUNICATION 6. STERIC EFFECTS IN ALKYLATIONS WITH QUATERNARY AMMONIUM SALTS, Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 11, November 1963, pp. 1977-1985.

The effect of steric factors on the formation  
 alkylation with quaternary ammonium salts containing the

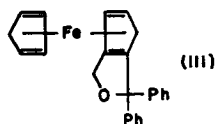
ferrocenylmethyl group was studied. Evidence is cited for the monomolecular mechanism of alkylation with ammonium salts containing a ferrocenylmethyl group. When methyl iodide acts on N-phenylferrocenemethylamine, N-methyl-N-phenylferrocenemethylamine, or  $\alpha$ -benzyl-N,N-dimethylferrocenemethylamine no quaternary salts are isolated, evidently as a result of considerable Brown Band F strain. Hydrolytic cleavage of salts  $[C_5H_5FeC_5H_4CH_2N^+(CH_3)_2R]X^-$  where R is n-alkyl showed increase in chain length of the group R causes a rate increase which is related to Brown Band F strain.

397. Popp, F. D. and Kirby, J. A.,  
FERROCENYLIDENE HYDRAZIDES, Journal of Chemical and Engineering Data, Vol. 8, No. 4, 1963, p. 604.

Ferrocenecarboxaldehyde (I) is treated with hydrazides in EtOH to give compounds of the general formula  $RCH:NN-HCOR'$  (II). A mixture of 0.005 mole I and 0.0055 mole hydrazide in absolute EtOH is refluxed 15 min., the mixture kept overnight, and the precipitate separated and recrystallized from aqueous EtOH to give the following II, where R =  $C_5H_5FeC_5H_4$  (R' m. p., and yield given): Ph, 186-7°, 83 percent; p-tolyl, 216°, 98 percent; p-tolyl, 208°, 55 percent;  $Ph_2C(OH)$ , 195-200°, 96 percent; Me, 196-7°, 69 percent,  $CH_2CN$ , 185-6°, 79 percent; cyclopropyl, 208-9°, 55 percent; pentamethylene, 143-5°, 62 percent; and the following II, where R = Ph (R', m. p., and yield given): cyclopropyl, 152°, 99 percent;  $C_5H_5FeC_5H_4$ , 187-8°, 69 percent.

398. Slocum, D. W., Rockett, B. W., and Hauser, C. R.,  
 RING METALATION OF DIMETHYLAMINOMETHYL-FERROCENE WITH BUTYLLITHIUM AND CONDENSATIONS WITH ELECTROPHILIC COMPOUNDS. SYNTHESIS OF 1,2-DISUBSTITUTED FERROCENES, American Chemical Society Journal, Vol. 87, No. 6, 1965, pp. 1241-1246.

N, N-Dimethylaminomethylferrocene (I) was metalated with BuLi in ether-hexane, and the resulting monolithioamine condensed with BzMe,  $Me_2CO$ , PhCN, and PhNCO, to form the corresponding 2-derivatives. The methiodide (II) of the BzMe adduct was cyclized by means of  $KNH_2$  to give the cyclic ether (III). II was also treated with KOH and KCN to afford the diol and carbinol nitrile, respectively. I was metalated with excess BuLi in tetrahydrofuran (THF)-hexane and the



resulting intermediates were condensed with BzMe to yield mainly the 2, 1'-derivatives; also some of the 2- and the 1'-derivatives were formed. These results furnish a route to the synthesis of a number of new 1,2-disubstituted and 1, 1', 2-trisubstituted ferrocenes. I underwent lithiation more readily than ferrocene. In THF-hexane, I was converted primarily into a dilithioamine. Some ir and nuclear magnetic resonance spectral correlations of 1,2-disubstituted ferrocenes are discussed.

399. Ustynyuk, Y. A. and Perevalova, E. G.,  
 REACTIVITY OF COMPOUNDS CONTAINING THE FERRO-  
 CENYLMETHYL GROUP, COMMUNICATION 7. REAR-  
 RANGEMENT OF BENZYL(FERROCENYLMETHYL)  
 DIMETHYL AMMONIUM CHLORIDE UNDER THE ACTION OF  
 NUCLEOPHILIC REAGENTS, Izvestiya Akademii Nauk SSSR,  
Seriya Khimicheskaya, No. 1, January 1964, pp. 62-69.

The rearrangements of benzyl (ferrocenylmethyl) dimethyl-  
 ammonium chloride under the action of benzyl magnesium  
 chloride and of N-butyl lithium in ether were studied. Also  
 the rearrangement with potassium amide in liquid ammonia  
 was studied. From these studies it was concluded that a  
 ferrocene nucleus stabilizes an adjacent carbanionic center  
 less strongly than a benzene ring does.

400. Ustynyuk, Y. A., Perevalova, E. G., and Nesmeyanov, A. N.,  
 REACTIVITY OF COMPOUNDS CONTAINING THE FERRO-  
 CENYLMETHYL GROUP. THE REARRANGEMENT OF  
 DIMETHYLBENZYL(FERROCENYLMETHYL) AMMONIUM  
 CHLORIDE UNDER THE INFLUENCE OF NUCLEOPHILIC  
 REAGENTS. VIII. WITTIG REARRANGEMENT IN THE  
 SERIES OF ETHERS OF FERROCENYLCARBINOL, Izvestiya  
Akademii Nauk SSSR, Seriya Khimicheskaya, No. 1, 1964,  
 pp. 62-73 (cf. CA 60, 6864f).

Dimethylbenzyl (ferrocenylmethyl) ammonium chloride  
 (I) treated with BuLi in Et<sub>2</sub>O under N gave after 5.5 hrs.,  
 followed by quenching in ice, 10 percent methylferrocene,  
 2.2 percent 1,2-diferrocenylethane, m. 200-200.5°, 42

percent ( $\alpha$ -phenyl- $\beta$ -ferrocenylethyl)dimethylamine (II).HCl, m. 227.5-8.5°, 8.4 percent N, N, N', N'-tetramethyl- $\alpha$ , $\beta$ -diphenylethylenediamine (IIa), m. 196.5°, and 30 percent residual II, b<sub>3</sub> 187-91°. The yield of II was reduced when BuLi was used in 100 percent excess, but the reaction gave appreciable  $\alpha$ -phenyl- $\beta$ -ferrocenylethylene (III), m. 118.5-9.5°, the yield of which rose to 17 percent when the mixture was also refluxed 6 hrs., after 22 hrs. at room temperature. I and KNH<sub>2</sub> in liquid NH<sub>3</sub> 3 hrs. gave 50 percent II and 2.5 percent 1,2-diferrocenylethane. I and PhCH<sub>2</sub>MgCl in Et<sub>2</sub>O, finally at reflux 20 hrs., gave 55 percent I (recovered as the iodide, decomposed 178-80°), 21 percent II, which was converted to the methiodide, decomposed 217-18°, and HCl salt, m. 225-6°. II and MeCN treated with MeI at 0° and kept 2 hrs. gave 72.8 percent II. MeI, m. 217-19°, which with Na-Hg in H<sub>2</sub>O, completed by refluxing 4 hrs., gave 57 percent 1-phenyl-2-ferrocenylethane, m. 58-9°. II. MeI refluxed with 0.1N NaOH gave 94 percent unreacted material, but in 4 hrs. in 0.6N NaOH gave a small yield of a red oil; refluxing in MeOH-NaOH 25 hrs. gave 50 percent unreacted salt and 42.6 percent III, m. 118.5-19.5°. II. MeI and KNH<sub>2</sub> in liquid NH<sub>3</sub> 3 hrs. gave 34.7 percent III and 4 unidentified amines. PhCH<sub>2</sub>NMe<sub>2</sub> refluxed 12 hrs. in the presence of (tert-BuO)<sub>2</sub> gave 52 percent unreacted amine and 16 percent IIa.

### VIII

Addition of BuLi in tetrahydrofuran to benzyl ferrocenylmethyl ether under N resulted in an exothermic reaction which after 4 hrs. at room temperature gave, after an aqueous treatment, 55 percent 1-phenyl-2-ferrocenylethanol, m. 82.5-84°, while the residue gave a yellow-red oil, b<sub>2</sub>, 160-5°, n<sub>D</sub><sup>20</sup> 1.5670, apparently amylferrocene, some 1,2-diferrocenylethane, m. 200-200.5°, and an unidentified red oil. Bis(ferrocenylmethyl) ether and BuCl in tetrahydrofuran similarly gave 26.6 percent starting material, 23.5 percent 1,2-diferrocenylethanol (I), m. 194.5-6.5°, and an unidentified red oil, b<sub>2</sub> 160-5°. I refluxed with Ac<sub>2</sub>O-KOAc 1 hr. gave 70 percent 1,2-diferrocenylethane, m. 264-5°, and 11 percent unreacted material. The products were characterized by their infrared spectra.



## E. Halogen Containing Ferrocene Derivatives

401. Hall, D. W. and Richards, J. H.,  
THE ACETYLATION OF SOME SUBSTITUTED FERROCENES,  
Journal of Organic Chemistry, Vol. 28, 1963, pp. 1549-1554.

A number of mono- and disubstituted ferrocenes have been acetylated. Iodine is lost from iodoferrocene under the acetylation conditions employed. Bromo- and chloroferrocenes are acetylated to give 1'-acetylbromo- (I) and chloroferrocenes in good yield. Acetylation of acetamido- and urethanoferrocenes gives predominantly the heteroannularly substituted isomers, and these substituents are deactivating.



402. Huffman, J. W., Keith, L. H., and Asbury, R. L., Jr.,  
SOME REACTIONS OF CHLORO FERROCENE WITH ORGANOLITHIUM COMPOUNDS, Journal of Organic Chemistry,  
Vol. 30, No. 5, 1965, pp. 1600-1604.

The reaction of chloroferrocene with butyllithium in hexane-tetrahydrofuran to afford butylferrocene, biferrocenyl, and some minor reaction products is reported. The same reaction when carried out in the presence of lithium piperidide affords also 1-ferrocenylpiperidine. The mechanism of these reactions is discussed.

403. Kauffmann, T., Henkler, H., and Zengel, H.,  
REDUCTIVE DEHALOGENATION WITH SODIUM HYDRAZIDE AND HYDRAZINE, Angewandte Chemie, Vol. 74, 1962,  
pp. 248-249.

Aromatic halides react rapidly in benzene or  $\text{Et}_2\text{O}$  solution with excess  $\text{NaNHNH}_2$  and  $\text{H}_2\text{NNH}_2$  (halide, reaction temperature, product, and percent yield given): mesityl bromide,  $25^\circ$ , mesitylene, 82; o-(m-, p-) bromoanisole,  $20^\circ$ , anisole, 58 (30, 38); 1(2)-bromonaphthalene,  $0^\circ$ , naphthalene, 75 (52); 1(2)-chloronaphthalene,  $0^\circ$ , naphthalene, 65 (75); 1(2)-fluoronaphthalene,  $25^\circ$  ( $0^\circ$ ), naphthalene, 39 (60); 9-bromoanthracene,  $0^\circ$ , anthracene, 90; 2,3-dibromocumarone,  $0^\circ$ , cumarone, 85; 2,3-dibromothionaphthene,  $45^\circ$ , thionaphthene, 74; 4-bromoisoquinoline,  $0^\circ$ , isoquinoline, 57; 1-chloroferrocene,  $30^\circ$ , ferrocene, 97.

404. Morrison, I. G. and Pauson, P. L.,  
DISPLACEMENT OF FERROCENE SUBSTITUENTS BY  
PROTONS, Chemical Society Proceedings, 1962, A 177.

A reverse substitution in an aromatic system involving electrophilic displacement of a substituent by a proton was observed in Friedel-Crafts acetylations of chloro- and methoxyferrocene (I and II), in which ferrocene (III) was produced in the former and acetylferrocene (IV) in the latter case. That III was a likely intermediate in the formation of IV was demonstrated when I, II, and methylthioferrocene (V) were found to give III on treatment with  $\text{AlCl}_3$  in  $\text{CH}_2\text{Cl}_2$  at room temperature under N. Dry HCl failed to dechlorinate I but HCl (formed from  $\text{AlCl}_3$  by traces of  $\text{H}_2\text{O}$ ) must play a part in the reaction. No dichloro derivative was isolated with I. II and V with  $\text{AlCl}_3$  gave not only III, but mixtures of the isomeric dimethoxy- and bis(methylthio)ferrocenes. A mechanism involving exchange of substituent and H in the known  $\text{AlCl}_3$  complex is postulated.

405. Nesmeyanov, A. N., Drozd, V. N., and Sazonova, V. A.,  
FERROCENE AZIDES, Doklady Akademii Nauk SSSR, Vol. 150, No. 2, 1963, pp. 321-324.

Refer to item No. 242 for abstract.

406. Nesmeyanov, A. N., Kursanov, D. N., Nefedova, M. N.,  
Setkina, V. N., and Perevalova, E. G.,  
REPLACEMENT OF HALOGEN IN HALO FERROCENES BY  
A PROTON, Doklady Akademii Nauk SSSR, Vol. 161, No. 6,  
1965, pp. 1349-1351 (In Russian).

Iodoferrocene and  $\text{CF}_3\text{CO}_2\text{D}$  in  $\text{C}_6\text{H}_6$  under N atm. gave a dark violet precipitate which was separated and the filtrate extracted with  $\text{H}_2\text{O}$  gave in the extract the evidence of ferricinium ion; treated with  $\text{Na}_2\text{SO}_3$  it gave ferrocene containing 9.5 percent D; the precipitate gave iodoferrocene, which with I gave the dark violet precipitate as above. Bromoferrocene similarly gave 10 percent ferrocene while chloroferrocene gave some chloroferrocene containing 25 percent D.

407. Nesmeyanov, A. N., Perevalova, E. G., Leonteva, L. I., and Ustynyuk, Y. A.,  
REACTIONS OF TRIFERROCENYLCHLOROMETHANE  
HYDROCHLORIDE, Izvestiya Akademii Nauk SSSR, Seriya  
Khimicheskaya, 1966, pp. 558-559 (In Russian).

Not abstracted.

408. Nesmeyanov, A. N., Perevalova, E. G., and Shilovtseva, L. S.,  
AMINOMETHYLATION OF PHENYL-, TOLYL-, AND CHLORO-  
FERROCENES, Izvestiya Akademii Nauk SSSR, Otdelenie  
Khimicheskikh Nauk, 1962, pp. 1767-1772 (cf. CA 56, 1477d).

The ferrocenes were aminomethylated by heating 12 hrs. at 110-15° with  $\text{CH}_2(\text{NMe}_2)_2$  in AcOH in the presence of  $\text{H}_3\text{PO}_4$  under N. The products after separation by chromatography on  $\text{Al}_2\text{O}_3$  saturated with  $\text{HCONH}_2$  were eluted with petr. ether and shown to consist of 5:1 mixtures of hetero- and homoannular products. They were also separated by paper chromatography using 30 percent  $\text{HCONH}_2$  in MeOH as the saturating solvent, with detection with KCNS. Typical  $R_f$  values of the products are tabulated. The following are reported: 1, 1'-(dimethylaminomethyl) phenylferrocene, decomposed 90-5° (homoannular isomer decomposed 143-5°); 1, 1-dimethylaminomethyl)-p-tolylferrocene, decomposed 167-70° [homoannular isomer decomposed 172-5° (sealed tube)]; 1, 1'-(dimethylaminomethyl)chloroferrocene, decomposed 185-90° (homoannular isomer decomposed 163-6°). Infrared spectra of the products were reported.

409. Nesmeyanov, A. N., Perevalova, E. G., Yuryeva, L. P., and Grandberg, K. I.,  
DIRECT CYANATION OF FERROCENE DERIVATIVES,  
Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh  
Nauk, 1962, pp. 1772-1777 (cf. CA 56, 1477d, 57, 9575c).

Refluxing 3.2 g. phenylferrocene with 5.8 g.  $\text{FeCl}_3$ , 60 ml. tetrahydrofuran, and 2 ml. liquid HCN, followed by 12 hrs. at room temperature, gave after dilution with  $\text{H}_2\text{O}$  and extraction with  $\text{Et}_2\text{O}$ , followed by chromatography on  $\text{Al}_2\text{O}_3$  with elution by petr. ether followed by petr. ether- $\text{C}_6\text{H}_6$ , 88.5 percent 1'-phenyl-1'-cyanoferrocene (i. e., homoannular product), a red oil. With  $\text{H}_2\text{O}_2$  in aqueous alcohol KOH this gave in 0.5 hr. heating 32 percent 1-phenyl-1-carboxamidoferrocene (homoannular product), m. 155.5-6.5° (with some

decomposition). Similar cyanation of bromoferrocene gave 78 percent bromocyanoferrocene, m. 91-2°. p-Nitrophenylferrocene gave p-nitrophenylcyanoferrocene, m. 134-5°; both of these were heteroannular products as indicated by the infrared spectra. Reaction of phenyl ferrocenyl sulfone was run with large excess  $\text{FeCl}_3$  and HCN for 10 hrs. and gave 52 percent cyanophenylsulfonylferrocene, m. 141-1.5°, which was also a heteroannular product. Acetylferrocene gave in 6.5 hrs. 18 percent acetylcyanoferrocene, m. 98-9° (2,4-dinitrophenylhydrazine decomposed 223-5°), which was also a heteroannular product. Nitroferrocene in 2 hrs. gave 3 percent cyanonitroferrocene, decomposed 188-9°, which was heteroannular. Cyanoferrocene gave 62 percent heteroannular dicyanoferrocene, m. 165.5-66° (in sealed tube), which was formed directly in 68 percent yield from 1.86 g. ferrocene, 16 g.  $\text{FeCl}_3$ , 6 ml. HCN, and 120 ml. tetrahydrofuran in 3 hrs. Competing cyanation of ferrocene and cyanoferrocene in 5 hrs. gave only traces of the dicyano derivative. Passage of  $\text{BF}_3$  into ferrocene and p-benzoquinone dissolved in  $\text{C}_6\text{H}_6$  gave  $\text{C}_{10}\text{H}_{10}\text{FeBF}_4$ , a violet solid. Ferricinium ferrichloride and  $\text{H}_2\text{PtCl}_6$  gave  $\text{C}_{20}\text{H}_{20}\text{Fe}_2\text{PtCl}_2$ , a blue-black solid. Ferricinium fluoroborate heated with HCN 2 hrs. in  $\text{H}_2\text{O}$  gave ferrocene and cyanoferrocene.

410. Nesmeyanov, A. N., Sazonova, V. A., and Drozd, V. N., INTRODUCTION OF AROMATIC AND HETEROCYCLIC RADICALS INTO FERROCENE. REACTION OF BROMOFERROCENE WITH ORGANOMAGNESIUM COMPOUNDS, (Foreign Title Not Available), Translated Into English by R. C. Taylor, U. S. Army Missile Command, Redstone Arsenal, Alabama, RSIC-573, June 1966 (Doklady Akademii Nauk SSSR, Vol. 165, No. 3, 1965, pp. 575-577 (In Russian)).

Refer to item No. 209 for abstract.

411. Nesmeyanov, A. N., Sazonova, V. A., and Drozd, V. N., SUBSTITUTION OF HALOGEN IN BROMOFERROCENE BY AROMATIC AND HETEROCYCLIC RADICALS, Doklady Akademii Nauk SSSR, Vol. 154, No. 1, 1964, pp. 158-159 (cf. CA 51, 9514b).

Heating 0.3 g. bromoferrocene (I) with 1.8 g.  $\text{Ph}_4\text{BCu.C}_5\text{H}_5\text{N}$  under N 0.5 hr. at 125-30° gave after extraction with  $\text{Et}_2\text{O}$  and chromatography on  $\text{Al}_2\text{O}_3$  in heptane 57 percent phenylferrocene; a 56 percent yield resulted from a similar reaction

with I and  $\text{Ph}_4\text{BK}$  in the presence of  $\text{Cu}_2\text{Br}_2$  moistened with pyridine. The reaction also gave some ferrocene (II), biferrocenyl, and probably polyphenylferrocenes. Similarly  $(p\text{-MeC}_6\text{H}_4)_4\text{BNa}$  and  $\text{Cu}_2\text{Br}_2$  gave 53 percent p-tolylferrocene, while tetra- $\alpha$ -thienylboropotassium gave 81 percent  $\alpha$ -thienylferrocene (III), m.  $116.5\text{-}17.5^\circ$ . Heating I with N-sodiopyrrole in the presence of  $\text{Cu}_2\text{Br}_2$  0.5 hr. at  $120^\circ$  gave some II, 17 percent N-pyrrolylferrocene, m.  $83\text{-}3.5^\circ$  (after sublimation in vacuo), and biferrocenyl. Tetra-1-indolylboropotassium similarly gave 35 percent N-indolylferrocene, m.  $89\text{-}90^\circ$ . Refluxing I with  $\text{PhC}\equiv\text{CCu}$  in  $\text{Me}_2\text{NCHO}$  3 hrs. under N gave 48 percent ferrocenylphenylacetylene, m.  $126\text{-}7^\circ$ .

#### F. Silicon, Sulfur, and Phosphorous Containing Ferrocene Derivatives

412. Drozd, V. N., Sazonova, V. A., and Nesmeyanov, A. N., FERROCENYL SULFONES. FERROCENYL MESITYL SULFONE UNDER THE CONDITIONS OF THE SMILES REARRANGEMENT, Doklady Akademii Nauk SSSR, Vol. 159, No. 3, 1964, pp. 591-594 (In Russian).

Keeping 0.9 g. bromoferrocene with 1.6 g. Cu benzene-sulfinate in  $\text{Me}_2\text{NCHO}$  2 days gave, after an aqueous treatment, 82 percent Ph ferrocenyl sulfone, m.  $153.5\text{-}54^\circ$ ; the yield was 78 percent after heating the mixture on a steam bath. Similarly, Cu ferrocenesulfinate gave 85 percent diferrocenyl sulfone, decomposed  $270\text{-}3^\circ$ , also formed in low yield from Cu ferrocenesulfinate kept alone in  $\text{Ph}_2\text{NCHO}$  2 days. Bromoferrocene and, Cu mesitylenesulfinate in  $\text{Me}_2\text{NCHO}$  2 days gave 7 percent mesityl ferrocenyl sulfone, m.  $148\text{-}9^\circ$ . Thiomesitylene was converted to the Cu salt and this with bromoferrocene in 40 min. at  $130^\circ$  gave 86 percent mesityl ferrocenyl sulfide, m.  $85.5\text{-}6.5^\circ$ , which with  $\text{H}_2\text{O}_2$  in  $\text{MeOH-KOH}$  at pH 7-9 in 25 hrs. gave 62 percent mesityl ferrocenyl sulfone (I) and 21 percent mesityl ferrocenyl sulfoxide, m.  $126\text{-}7^\circ$ . I and  $\text{BuLi}$  in  $\text{Et}_2\text{O}$  overnight gave Li ferrocenesulfinate.

413. Nesmeyanov, A. N., Drozd, V. N., Sazonova, V. A., Romanenkov, V. I., Prokof'ev, A. K., and Nikonova, L. A.,  
DIFFEROCENYLS AND TERFERROCENYLS, Izvestiya Akademii Nauk SSSR, Otdeline Khimicheskikh Nauk, 1963, pp. 667-674.

Refer to item No. 119 for abstract.

414. Nesmeyanov, A. N., Kursanov, D. N., Vil'chevskaya, V. D., Kochetkova, N. S., Setkina, V. N., and Novikov, Y. N.,  
REACTIONS OF TRIFERROCENYLPHOSPHINE OXIDE, Doklady Akademii Nauk SSSR, Vol. 160, No. 5, 1965, pp. 1090-1092 (In Russian).

$[(C_5H_5)_2Fe]_3PO$  (I) kept in  $Ac_2O$  with concentrated  $H_2SO_4$  20 hrs. gave a trisulfonic acid trihydrate, a hygroscopic solid, soluble in  $H_2O$  and alkalies, from which it was precipitated by acids. Treated with  $CH_2N_2$  it gave the tri-Me ester dihydrate, m. 118-20°. I in concentrated  $H_2SO_4$  12 hrs. gave on dilution a yellow solid, identified as diferrocenylphosphinic acid and a solid,  $C_{20}H_{19}Fe_2PO_5S \cdot 1.5H_2O$ , separated by solution in  $C_6H_6$ . I and  $CF_3CO_2D$  under N atm. were found to undergo D-H exchange at the rate of  $1.6 \times 10^{-7} \text{ sec.}^{-1}$  at 25°,  $4.4 \times 10^{-7}$  at 35°, and  $12.8 \times 10^{-7}$  at 45°, assuming exchange participation of all 27 H atoms in I. The strong electronacceptor action of the PO group was noted in this reaction. Most of D was located in unsubstituted cyclopentadienyl rings. The sulfo groups in the sulfonic acid were probably located in different rings.

415. Nesmeyanov, A. N., Perevalova, E. G., Churanov, S. S., and Nesmeyanova, O. A.,  
REACTIONS OF FERROCENESULFONIC ACIDS, Doklady Akademii Nauk SSSR, Vol. 119, 1958, pp. 949-952 (cf. CA 52, 368b).

Heating 12 g. Pb ferrocenedisulfonate with 30 ml.  $POCl_3$  40 min., pouring the mixture on ice, and extracting with  $(CH_2Cl)_2$  gave on evaporation of the extraction 64 percent ferrocenedisulfonyl chloride (I), yellow-orange, decompose 150° (with flame). Heating 2.9 g. Pb ferrocenedisulfonate with 20 ml.  $PCl_3$  1 hr., scpg. the precipitate, heating this with 10 ml.  $PCl_3$  in  $(CH_2Cl)_2$ , and evaporating the organic solutions gave 36 percent ferrocenedisulfonic acid monochloride, yellow, decomposition 129°, sparingly soluble in  $H_2O$ . Heating Pb ferrocenesulfonic acid with  $PCl_3$  3-5 min. and pouring on ice

gave a reddish precipitate characteristic of the monosulfonic acid; the disulfonic acid gives a yellow solution. With  $\text{POCl}_3$ , the disulfonic acid yields a precipitate on aqueous treatment while the monosulfonic acid gives a green solution. I refluxed with  $\text{Et}_2\text{NH}$  gave 92 percent yellow ferrocenebis(diethylsulfonamide), m.  $159-61^\circ$  (from  $\text{EtOAc}$ ). Similarly was prepared ferrocenediethylsulfonamide, yellow, m.  $91-2^\circ$ . Refluxing ferrocenemonosulfonyl chloride with Zn dust in aqueous  $\text{Et}_2\text{O}$  1 hr. and heating the product with aqueous  $\text{Na}_2\text{CO}_3$  gave Na ferrocenesulfinate dihydrate (from  $\text{H}_2\text{O}$ ). Reduction of the ferrocenemonosulfonyl chloride with excess  $\text{LiAlH}_4$  and treatment of the resulting crude thioferrocenol with  $\text{NaOH}$  and  $\text{Cl-CH}_2\text{OC}_2\text{H}$  gave 56 percent S-ferrocenylthioglycolic acid, m.  $109-10^\circ$  (from aqueous  $\text{EtOH}$ ), and some differocenyl disulfide. The latter was prepared by similar reduction of the sulfonyl chloride by evaporation of the solvent. Reduction of the disulfide with  $\text{LiAlH}_4$  and treatment of the product with  $\text{NaOH-BzCl}$  gave 92 percent thioferrocenyl benzoate, m.  $138-9^\circ$ . Heating ferrocenedisulfonic acid with  $\text{H}_2\text{O}$  at  $100^\circ$  6 hrs. gave, after precipitation of Fe with  $\text{NH}_4\text{OH}$ , the indication that 26 percent of the initial material has been destroyed. Infrared spectra of the new S-derivatives of ferrocene are reported.

416. Petrov, A. D., Sokolova, E. B., Shebanova, M. P., and Golovina, N. I.,  
 ADDITION OF SILICON HYDRIDES TO DIMETHYLALLYL-FERROCENYLSILANE IN THE PRESENCE OF  $\text{H}_2\text{PtCl}_6$ ,  
Doklady Akademii Nauk SSSR, Vol. 152, No. 5, 1963, pp. 1118-1121.

$\text{BuLi}$  and ferrocene in  $\text{Et}_2\text{O}$  refluxed 10 hrs. under N and treated with 1 mole  $\text{CH}_2\text{:CHCH}_2\text{SiMe}_2\text{Cl}$  at reflux 15 hrs., gave after an aqueous treatment dimethylallylferrocenylsilane (I), f.p.  $-61^\circ$ ,  $n_D^{20}$  1.5570,  $d_{20}$  1.0889. I and  $\text{MeEt}_2\text{SiH}$  in the presence of  $\text{H}_2\text{PtCl}_6$  in iso- $\text{PrOH}$  gave red-brown ferrocenyl-dimethyl [ $\gamma$ -(methyldiethylsilyl)propyl] silane, 56 percent, 1.5387, 1.0558. Similarly were prepared: ferrocenyldimethyl [ $\gamma$ -(triethylsilyl)propyl] silane, 57.5 percent, 1.5402, 1.0512; ferrocenyldimethyl [ $\gamma$ -(methyldibutylsilyl)propyl] silane, 67.7 percent, 1.5173, 0.985; ferrocenyldimethyl [ $\gamma$ -(methylethylchlorosilyl)propyl] silane (II), 93.2 percent, 1.5421, 1.1250; ferrocenyldimethyl [ $\gamma$ -(methyldichlorosilyl)propyl] silane, 98.3 percent, 1.5389, 1.2046. All were reddish liquids with low freezing points. Hydrolysis of II gave a siloxane, 20 percent, 1.5582, 1.1302, and ferrocene. The products were characterized by their infrared spectra.

417. Pitman-Dunn Institute for Research, Frankfort Arsenal, Philadelphia, Pennsylvania,  
FERROCENYLPHOSPHONOUS DICHLORIDE FROM FERROCENYLPHOSPHINIC ACID. THE PH(O) - P(OH) TAUTOMERISM by G. P. Sollott and E. Howard, Jr., Report No. AFA A64 18, AD-450 147, Contract No. DA 1A010501B010 (Unclassified Report) (Journal of Organic Chemistry, Vol. 29, 1964, pp. 2451-2452).

Ferrocenylphosphinic acid is converted to ferrocenylphosphonous dichloride by reaction with a large excess of phosphorus trichloride. This is considered to be evidence that the phosphinic acid exists in tautomeric equilibrium with the phosphonous acid form, the preparation of ferrocenylphosphonous dipiperide, the first known phosphorus amide of ferrocene, is reported.

418. Smalley, A. W.,  
THE EFFECT OF FERROCENYL GROUPS ON THE DECOMPOSITION OF QUATERNARY PHOSPHONIUM HYDROXIDES, University Microfilms (Ann Arbor, Michigan), Order No. 66-537, 97 pp., Dissertation Abstract, Vol. 26, No. 10, 1966, p. 5727.

The effect of the halide anion on the rate of decomposition of triphenylbenzylphosphonium iodide and chloride with alkali has been investigated. Whereas the difference in rates between the iodide and chloride in 50 percent 1,2-dimethoxyethane-water was not too marked, a profound difference in the rates of decomposition between the two halides was noted for reactions carried out in 50 percent methanol-water solution. These results are tentatively explained on the basis of the difference in nucleophilicity of the halide anions, the difference in polarities of 1,2-dimethoxyethane-water, and on the basis of a common ion rate depression effect operative in these media.

Ferrocenyldiphenylbenzylphosphonium iodide, diferrocenylphenylbenzylphosphonium iodide and triferrocenylbenzylphosphonium iodide have been prepared and subjected to the decomposition reaction with sodium hydroxide. The reactions have been found to follow a third-order rate law, as did previous alkaline decomposition reactions of quaternary phosphonium hydroxides; however, a marked decrease in the rate of decomposition was noted as the number of ferrocenyl groups was increased. From product ratio studies it was also found that ferrocene was formed in substantial amount in the aqueous



alkaline decompositions of ferrocenyl substituted quaternary phosphonium halides, although toluene was the major hydrocarbon product in each case. An intermediate of high reactivity and low selectivity is proposed to explain these results.

419. Sollott, G. P. and Howard, E., Jr.,  
FERROCENYLPHOSPHONOUS DICHLORIDE FROM FERROCENYLPHOSPHINIC ACIDS. THE  $> \text{PH}(\text{O}) \rightleftharpoons > \text{P}(\text{OH})$  TAUTOMERISM, Journal of Organic Chemistry, Vol. 29, No. 8, 1964, pp. 2451-2452.

The method of Frank (CA 55, 23403i) was applicable to the conversion of ferrocenylphosphinic acid to ferrocenylphosphonous dichloride (I). The results indicated an equilibrium-involving form  $\text{ArP}(\text{OH})_2$ . I could not be distilled but was identified by hydrolysis to the phosphinic acid and conversion into ferrocenylphosphonous dipiperidide (II). II was the first known phosphorus amide of ferrocene. Infrared spectra of I and II were obtained.

420. Bach, J. L.,

PART I. REACTION OF THE TRIPHENYLMETHYL RADICAL WITH THE ISOMERIC XYLENES AND TOLUENE, PART II. THE METALATION OF THE ALKYLFERROCENES WITH *n*-AMYLSODIUM, University Microfilms (Ann Arbor, Michigan), Order No. 64-4561, 101 pp., Dissertation Abstract, Vol. 25, No. 2, 1964, p. 824.

## PART I

The reaction of the triphenylmethyl radical with the isomeric xylenes was shown to have formed 1,1,1-triphenyl-2 (tolyl) ethanes. These products were contrary to those reported by H. Wieland who claimed to have isolated the xylyl-triphenylmethanes from this reaction. Toluene was also tritylated under conditions similar to the xylenes and yielded 1,1,1,2-tetraphenylethane.

Thus, the radical attack occurs on an alpha hydrogen rather than on a nuclear hydrogen in all of these reactions.

## PART II

Methyl, ethyl and isopropylferrocene were prepared by a lithium aluminum hydride-aluminum chloride reduction of the corresponding alcohols. *t*-Butylferrocene was synthesized in high yields by a Friedel-Crafts alkylation of ferrocene.

When the alkylferrocenes thus prepared were metalated with *n*-amylsodium (1:1 ratio) both mono and dimetalation occurred. The monometalated fraction was shown to contain the 1,3 and 1,1' isomers in a ratio of 30:70 percent in all cases. Since the ratio of these products calculated from a statistical approach was 28:72 percent, it was concluded that the acidity of the hydrogen in the three position relative to the alkyl group was about the same as that of a hydrogen in the unsubstituted ring.

The dimetalated fraction was composed of two compounds having the 1,2,1' and 1,3,1' structure. The percentage of 1,2,1' compound was greatest in the case of methylferrocene (11 percent), 5 percent for ethyl ferrocene and became insignificant for both isopropyl and *t*-butylferrocene. The dominant force in determining this product distribution was thought to be the steric effect of the alkyl group.

In all of these metalations, as in the metalation of ferrocene with *n*-amylsodium, the dimetalated fraction was present

as the major component (70 percent). From both a mass law effect and a statistical distribution, one would predict that only a small amount of dimetalated compound would be formed. It was concluded from these data that, at the very least, the dianion should be as stable as the monoanion and very likely is more stable.

Ferrocene and isopropylferrocene were also metalated with n-butyllithium (1:1 ratio) and, in both cases, a preponderance of monometalation (60 percent) was found. In contrast to the reactions with n-amylsodium, these metalations were shown to be homogeneous. Here, as in the case of the n-amylsodium metalations, the dimetalated compound was formed in larger amounts than expected. It is therefore suggested that the dianion is more stable than the monoanion.

In a competitive metalation between equimolar quantities of benzene and ferrocene, an insignificant amount of methyl benzoate was formed. Thus, ferrocene is more reactive to electrophilic attack and to metalation than benzene.

Nuclear magnetic resonance spectra of some 2- and 3-alkyl-1,1'-dicarbomethoxyferrocenes were measured. The 1,2 structure was easily distinguished from that of the 1,3 by measuring the relative areas of the ring protons. A larger chemical shift was found for the protons alpha to the carbomethoxy group than those beta to it. The 1,2 structure always showed one alpha proton and two beta protons (reversed in the case of the 1,3 structure) for the disubstituted ring. Thus, measurement of the peak area of the ring protons distinguished the structure of these isomers.

421. Duke University, Durham, North Carolina,  
CERTAIN REACTIONS OF ORGANOMETALLIC COMPOUNDS  
AND SOME CYCLIZATIONS, FINAL REPORT, SEPTEMBER  
1, 1955-DECEMBER 31, 1962 by C. R. Hauser, 1962, Report  
No. AROD-1443-55, Contract No. DA-36-034-ORD-2040,  
N63-12217 (Unclassified Report).

Results of studies on certain reactions of organometallic compounds and some cyclizations during the period 1 September 1955 to 31 December 1962, are summarized.

422. Duke University, Durham, North Carolina,  
RING METALATION OF DIMETHYLAMINOMETHYL-  
FERROCENE WITH BUTYL LITHIUM AND CONDENSATIONS  
WITH ELECTROPHILIC COMPOUNDS. SYNTHESIS OF 1,2-  
DISUBSTITUTED FERROCENES by D. W. Slocum, B. W.  
Rockett and C. R. Hauser, September 1964, Report No. AROD  
3581:7, AD-614 544, Contract No. DA-ARO-D31-124G409  
(Unclassified Report), (American Chemical Society Journal,  
Vol. 87, No. 6, 1965, pp. 1241-1246).

N, N-Dimethylaminomethylferrocene (I) was metalated with N-butyllithium in ether-hexane, and the resulting monolithioamine was condensed with benzophenone, acetone, benzonitrile, and phenyl isocyanate to form the corresponding 2-derivatives. The methiodide (II) of the benzophenone adduct was cyclized by means of potassium amide to give the cyclic ether.

Methiodide II was also treated with potassium hydroxide and potassium cyanide to afford the diol and carbinol-nitrile, respectively. Amine I was metalated with excess N-butyllithium in THF-hexane and the resulting intermediates were condensed with benzophenone to yield mainly the 2,1'-derivative; also some of the 2- and the 1'-derivatives were formed. These results furnish a route to the synthesis of a number of new 1,2-disubstituted and 1,2,1'-trisubstituted ferrocenes. Amine I underwent lithiation more readily than ferrocene. In THF-hexane, amine I was converted primarily to a dilithioamine.

Some infrared and nuclear magnetic resonance spectral correlations of 1,2-disubstituted ferrocenes are discussed.

423. Little, W. F., Clark, A. K., Benner, G. S., and Noe, C.,  
GRIGNARD REAGENTS OF p-AND m-BROMOPHENYL-  
FERROCENE, Journal of Organic Chemistry, Vol. 29, No.  
3, 1964, pp. 713-714.

The Grignard reagent of p-bromophenylferrocene has been prepared in tetrahydrofuran (THF), accompanied by the formation of phenylferrocene, and has been found to react normally with  $H_2O$ ,  $CO_2$  and BzPh. Attempts to prepare the reagent at higher temperatures in dimethylcarbitol yielded only phenylferrocene and p,p'-diferrocenylobiphenyl. Similarly, m-bromophenylferrocene reacted with Mg at high temperatures in dimethylcarbitol to yield only phenylferrocene and m,m'-diferrocenylobiphenyl, but even at lower temperatures in THF only these 2 products could be obtained.

24. Monsanto Chemical Company, Research and Engineering Division, Everett, Massachusetts, DERIVATIVES OF FERROCENE. PART I. METALATION OF FERROCENE by M. D. Rausch, M. Vogel, and H. Rosenberg, Charles J. Cleary Awards for Papers on Material Sciences, Washington, D. C., Library of Congress, Science and Technology Division, 1962, N63-13241, N63-13234 07-01, pp. 101-115 (Unclassified Report).

The metalation of ferrocene by means of n-butyl-lithium and mercuric acetate has been further investigated. The lithiation reaction has been extended for the preparation of trimethylsilylferrocene and 1, 1'-di(trimethylsilyl)ferrocene. In the mercuration reaction, the ratio of starting materials has been varied in order to obtain optimum yields of either chloromercuriferrocene or 1, 1'-dichloromercuriferrocene. Chloromercuriferrocene has been converted to diferrocenylmercury by means of dispersed sodium, sodium stannite, and sodium iodide in ethanol.

425. Nefedov, V. A. and Nefedova, M. N., SYNTHESSES BASED ON ORGANIC DERIVATIVES OF MERCURY. I. REACTION OF MERCURATED FERROCENES WITH COPPER SALTS, Zhurnal Obshchei Khimii, Vol. 36, No. 1, 1966, pp. 122-126 (In Russian).

Mercurated products of ferrocene were separated as follows; dilution of the reaction mixture with  $H_2O$  gave ferrocenylmercuric acetate, m. 115-16°; treatment with KBr gave bromomercuriferrocene, decomposed at 184-6°, after extraction with  $(CH_2Cl)_2$  and treatment of the extracted material with petroleum ether. Extraction of the crude products with  $Me_2CO$  gave 1, 3-bis(bromomercuri)ferrocene, a yellow powder. Chloromercuriferrocene heated in  $Me_2CO$  with  $CuCl_2 \cdot 2H_2O$  and  $H_2O$  10 min. gave 58 percent chloroferrocene, m. 58-9°.  $CuBr_2$  similarly gave 69 percent bromoferrocene, m. 32-3°. 1, 1'-Bis(chloromercuri)ferrocene and  $CuCl_2$  similarly gave 17 percent 1, 1'-dichloroferrocene, m. 75-7°, and 1-chloro-1'-chloromercuriferrocene, m. 141-3°, separated on  $Al_2O_3$  by elution with  $C_6H_6$  and heptane. Similarly prepared was 1, 1'-dibromoferrocene, m. 50°. Bromomercuriferrocene and  $Cu(OAc)_2$  heated to 130° in vacuo 2 hrs. gave 2 percent acetoxyferrocene, m. 63-4°; similarly chloromercuriferrocene and  $Cu$  phthalimide gave 4 percent N-ferrocenylphthalimide m. 152-4°. Dibromoferrocene heated with  $PhOK$  in the presence

of powdered Cu in xylene 40 min. gave 20 percent 1,1'-diphenoxyferrocene, m. 90.5-91°; bromoferrocene similarly gave phenoxyferrocene, m. 87-8°. 1,1'-bis(chloromercurio)ferrocene and  $\text{Cu}(\text{SCN})_2$  heated 6 hrs. in  $\text{C}_6\text{H}_6$  gave 30 percent thiocyanoferrocene m. 97-8°, and 1,1'-dithiocyanoferrocene, m. 114-15°. The former and  $\text{MeMgI}$  gave 90 percent methylthioferrocene (I),  $n_D^{25}$  1.6488; methiodide, m. 106-7°. Similarly prepared was 1,1'-bis(methylthio)ferrocene, a liquid. I oxidized with  $\text{H}_2\text{O}_2$  gave the sulfone, m. 73-4°.

426. Nesmeyanov, A. N., Anisimov, K. N., Kolobova, N. E., and Magomedov, G. K. I.,  
ISOMERIZATION OF TERTIARY  $\beta$ -ACETYLENIC ALCOHOLS, DERIVATIVES OF CYCLOPENTADIENYLMANGANESE TRICARBONYL AND FERROCENE, Doklady Akademii Nauk SSSR, Vol. 163, No. 5, 1965, pp. 1159-1162 (In Russian).

The conventional Grignard reaction was used to prepare alcohols:  $\text{C}_5\text{H}_5\text{FeC}_5\text{H}_4\text{CMe}(\text{OH})\text{CH}_2\text{C}\equiv\text{CH}$ ,  $b_{0.006}$  92.5°,  $n_D^{20}$  1.6092,  $d_{20}$  1.2878;  $(\text{CO})_3\text{MnC}_5\text{H}_4\text{C}(\text{Et})(\text{OH})\text{CH}_2\text{C}\equiv\text{CH}$ ,  $b_{0.006}$  65-7°, 1.5782, 1.3270;  $(\text{CO})_3\text{MnC}_5\text{H}_4\text{CPh}(\text{OH})\text{CH}_2\text{C}\equiv\text{CH}$ , m. 84-5°. These heated in vacuo with  $\text{KHSO}_4$  or in tetrahydrofuran with  $\text{P}_2\text{O}_5$  isomerized to 93-6 percent ketones:  $\text{C}_5\text{H}_5\text{FeC}_5\text{H}_4\text{CMe}:\text{CHCOMe}$ , m. 89-90° (2,4-dinitrophenylhydrazone m. 150°);  $(\text{CO})_3\text{MnC}_5\text{H}_4\text{C}(\text{Et}):\text{CHCOMe}$ , m. 69° (2,4-dinitrophenylhydrazone m. 205°);  $(\text{CO})_3\text{MnC}_5\text{H}_4\text{CPh}:\text{CHCOMe}$ , m. 73-4° (2,4-dinitrophenylhydrazone m. 201-3°). The second alcohol isomerized best with  $\text{HgSO}_4$  in hot EtOH, while the third alcohol isomerized with  $\text{HgSO}_4$  in warm EtOH, while the first alcohol isomerized under these conditions at room temperature. Also reported was  $(\text{CO})_3\text{MnC}_5\text{H}_4\text{CPh}(\text{OH})\text{CH}_2\text{COMe}$ , m. 97°.

427. Nesmeyanov, A. N., Perevalova, E. G. and Nesmeyanova, O. A.,  
MECHANISM OF FORMATION OF FERROCENE IN ELECTROPHILIC AND HOMOLYTIC REACTIONS OF IODOFERROCENE AND MERCURY DERIVATIVES OF FERROCENE. Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, 1962, pp. 47-52 (cf. CA 54, 21027a).

Ferrocene was one of the products of diferrocenylmercury with Na,  $\text{SnCl}_2$ ,  $\text{CuCl}_2$ ,  $\text{CCl}_4$ . This substance evidently formed from a ferrocenyl radical which had a remarkable selectivity for removal of H and removed this atom not only from the solvent but even from the initial ferrocene compound. A

similar explanation was applicable to some reactions of iodoferrocene. Diferrocenylmercury and Na in hot  $C_6H_6$  under N 15 hrs. gave 10 percent ferrocene. Similar reaction with  $SnCl_2$  in petr. ether in 15 hrs. gave 15.5 percent ferrocene, while a reaction with  $CuCl_2$  in dioxane in 1 hr. gave some chloroferrocene and 5 to 7 percent ferrocene, estimated after chromatographic separation on  $Al_2O_3$ . Symmetrized 1,1'-bis(chloromercuri) ferrocene refluxed with  $CuCl_2 \cdot 2H_2O$  in  $C_6H_6$ -dioxane 2 hrs. gave a mixture of ferrocene and dichloroferrocene, m. 80-110°. Heating diferrocenylmercury with dry  $C_6H_6$  resulted in no evidence of reaction, however, a similar reaction in  $CCl_4$  6 hrs. gave 57 percent chloromercuriferrocene, 22 percent ferrocene, and a resin containing 10 percent Hg, 10.6 percent Fe, C, H, and Cl. A product with lower Fe content was formed by a similar reaction, followed by treatment with hot HCl or aqueous  $Na_2S_2O_3$ . Heating diferrocenylmercury in  $CCl_4$  in the presence of hydroquinone 6 hrs. gave 12.5 percent ferrocene; similar reaction in the presence of  $Bz_2O_2$  gave 3 percent ferrocene and 85 percent unreacted material; no chloromercuriferrocene was detected. Heating diferrocenylmercury with ferrocenesulfonyl iodide in  $C_6H_6$  4 hrs. gave 23 percent ferrocene and 27 percent diferrocenyl sulfone. Na ferrocenesulfinate and iodine in  $H_2O$ -EtOH gave a solution of unstable ferrocenesulfonyl iodide, which was extracted with  $C_6H_6$  (red solution) and could be used only in solution, as the iodide decomposed immediately upon removal of the solvent.

428. Nesmeyanov, A. N., Perevalova, E. G., and Nesmeyanova, O. A.,

REACTIONS OF DIFERROCENYLMERCURY, Doklady Akademii Nauk SSSR, Vol. 119, 1958, pp. 288-291.

Refluxing diferrocenylmercury (I) with  $Ph_3CCl$  in  $C_6H_6$  4 hrs. gave a green precipitate which, treated with  $Na_2S_2O_3$ , solution in  $Et_2O$ , chromatographed on  $Al_2O_2$ , and eluted with petr. ether, gave some 1 percent ferrocene (II), an unidentified oil, and 18 percent ferrocenyltriphenylmethane, m. 179-81° (BuOH). I with excess  $PhSO_2I$  in  $C_6H_6$  gave overnight some II, some 27 percent I, and 22 percent ferrocenyl Ph sulfone, m. 145-6° (EtOH). Refluxing I with ferrocenesulfonyl chloride in  $C_6H_6$  18 hrs. gave 35 percent II, some starting material, and 6 percent diferrocenyl sulfone, decomposed 270-5° (BuOH). I and  $AcCl$  refluxed 5 hrs. in  $C_6H_6$  gave 1,1 percent acetylferrocene, m. 82-4°. Trituration of I with

an alcohol, extract of a reaction mixture of  $\text{CuSO}_4$  and  $\text{KSCN}$ , heating 15 min., and treatment 3 hrs. with aqueous  $\text{Na}_2\text{S}_2\text{O}_3$  gave 25 percent II and 15 percent diferrocenyl disulfide, m. 185-7° (EtOH). Treatment of I with  $\text{SeBr}_4$  in  $\text{CHCl}_3$  1 hr. at reflux gave after treatment of the residue several days with aqueous  $\text{Na}_2\text{S}_2\text{O}_3$  21 percent diferrocenyl selenide, m. 151-3° (iso-BuOH and EtOH).

429. Nesmeyanov, A. N., Sazonova, V. A., and Gerasimenko, A. V.,  $\alpha$ -PYRIDYLFERROCENE AND 1,1'-di( $\alpha$ -PYRIDYL) FERROCENE, Doklady Akademii Nauk SSSR, Vol. 147, 1962, pp. 634-635.

See item No. 249 for abstract.

430. Nesmeyanov, A. N., Sazonova, V. A., Gerasimenko, A. V., and Medvedeva, V. G., REACTION OF FERROCENEBORONIC ACIDS WITH COPPER PHTHALIMIDE, Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk, 1962, pp. 2073-2074 (cf. CA 54,12089e).

Heating ferroceneboronic acid with Cu phthalimide in pyridine 10 min., followed by adding  $\text{Et}_2\text{O}$ , separating precipitated Cu salts, and washing the organic layer with aqueous NaOH and AcOH gave 47 percent N-ferrocenylphthalimide (I) m. 156-6.5°, after chromatographic purification on  $\text{Al}_2\text{O}_3$ . Similarly, 1,1'-ferrocenylenediboronic acid gave 29 percent I, along with minor amounts of ferrocene and diferrocenyl.  $\text{PhCH:CHB(OH)}_2$  and Cu phthalimide similarly gave 56 percent N- $\beta$ -styrylphthalimide, m. 185-6°.  $\text{PhB(OH)}_2$  similarly gave 19 percent N-phenylphthalimide, while p- $\text{MeOC}_6\text{H}_4\text{B(OH)}_2$  gave 34 percent N-p-anisylphthalimide, m. 159.5-60.5°.

431. Nesmeyanov, A. N., Sazonova, V. A., Romanenko, V. I. Rodionova, N. A., and Zol'nikova, G. P., PHOTOLYSIS OF FERROCENE DERIVATIVES, Doklady Akademii Nauk SSSR, Vol. 155, No. 5, 1964, pp. 1130-1133.

See item No. 252 for abstract.



432. Perevalova, E. G. and Ustynyuk, Y. A.  
REACTIVITY OF COMPOUNDS CONTAINING THE FERRO-  
CENYLMETHYL GROUP. III. REACTIONS OF QUATERNARY  
AMMONIUM SALTS CONTAINING THE FERROCENYLMETHYL  
RADICAL WITH ORGANOMAGNESIUM COMPOUNDS IN THE  
PRESENCE OF COBALT CHLORIDE. Izvestiya Akademii  
Nauk SSSR, Seriya Khimicheskaya, No. 10, October 1963,  
pp. 1776-1782 (cf. CA 59, 7557b).

Refer to item No. 393 for abstract

433. Perevalova, E. G., Ustynyuk, Y. A., and Nesmeyanov, A. N.  
REACTIVITY OF COMPOUNDS CONTAINING THE FERRO-  
CENYLMETHYL GROUP, COMMUNICATION 4. REACTIONS  
OF FERROCENYLMETHYLLITHIUM. Izvestiya Akademii  
Nauk SSSR, Seriya Khimicheskaya, No. 11, November 1963,  
pp. 1967-1972.

The preparation of ferrocenylmethyl lithium is described. Its reactions with formaldehyde, benzaldehyde, and carbon dioxide are described. Ferrocenylmethyl lithium with formaldehyde gives 2-ferrocenylethanol, with benzaldehyde 1-phenyl-2-ferrocenyl-1-ethanol is formed, and with carbon-dioxide alpha ferrocenylacetic acid is formed. In all cases the main side product is methyl ferrocene.

434. Perevalova, E. G., Ustynyuk, Y. A., Nesmeyanov, A. N., and Ustynyuk, L. A.,  
REACTIVITY OF COMPOUNDS CONTAINING THE FERRO-  
CENYLMETHYL GROUP. IV. REACTIONS OF FERROCENYL-  
METHYLLITHIUM. V. PREPARATION OF ORGANOLITHIUM  
COMPOUNDS WITH  $\alpha$ -FERROCENYLALKYL GROUPS. VI.  
STERIC EFFECTS IN ALKYLATION REACTIONS OF  
QUATERNARY AMMONIUM SALTS, Izvestiya Akademii Nauk  
SSSR, Seriya Khimicheskaya, No. 11, 1963, pp. 1967-1985  
(cf. Lednicer, CA 53, 11331g; Perevalova and Ustynyuk, CA 60, 5549f).

Ferrocenylmethyllithium (I) solution from Li and ferrocenylcarbinyl Me ether in tetrahydrofuran (THF) was treated with paraformaldehyde 1 hr. at  $-5^{\circ}$  and 3 hrs. at room temperature to give 57 percent  $\beta$ -ferrocenylethyl alcohol, m.  $39-40^{\circ}$ ; 28 percent methylferrocene m.  $35-6.5^{\circ}$ ; and some 1,2-differocenylethane, m.  $200-200.5^{\circ}$ . The alcohol kept in sunlight in a closed flask 1 week changed its m. p. to  $47-9^{\circ}$ ;

this was evidently a crystalline modification. The alcohol and BzCl in pyridine gave 73 percent the benzoate, m. 73.5-75°. I and BzH gave 73 percent 1-phenyl-2-ferrocenylethanol (II), m. 82.5-84°, 32 percent methylferrocene, and some diferrocenylethane. II and Ac<sub>2</sub>O-NaOAc refluxed 1 hr. under N gave 92 percent II acetate, m. 99-100°, which at 300° under N gave 60 percent 1-phenyl 2-ferrocenylethane (III), m. 118.5-119.5°. PhCH<sub>2</sub>MgCl and ferrocenecarboxaldehyde in Et<sub>2</sub>O gave 84.5 percent 2-phenyl-1-ferrocenylethanol, m. 81-2°, which with Ac<sub>2</sub>O-KOAc at reflux 1 hr. under N gave 99 percent III. I and CO<sub>2</sub> gas gave 45 percent methylferrocene, some 1,2-diferrocenylethane, and 48 percent ferrocenylacetic acid, m. 165-7°, after sublimation in vacuo. The yield of this acid dropped to 18-25 percent when dry ice was used instead of gaseous CO<sub>2</sub> in the above reaction; the yield of methylferrocene rose to 58-60 percent and that of diferrocenylethane to 4-8 percent. Heating the crude acid in cyclohexane or Et<sub>2</sub>O-petr. ether gave an amorphous solid, m. > 250°, which dissolved with color development similar to that of ferricinium salts in dilute HCl; treatment of the solution with SnCl<sub>2</sub> gave a yellow color extractable with Et<sub>2</sub>O; treated with aqueous KOH and acidified, the mixture gave ferrocenylacetic acid; evidently the acid is oxidized by O to an inner salt.

## V

Addition of 2.07 g. bis(ferrocenylmethyl) ether in THF to 0.7 g. Li shavings under the same solvent at -5° under N, followed by 1 hr. at room temperature, gave 75 percent methylferrocene, 1,2-diferrocenylethane, m. 200-200.5°, starting material, and 82.5 percent ferrocenylcarbinol, m. 80-1°. Similar treatment of benzyl ferrocenylmethyl ether gave 57 percent methylferrocene; 2.2 percent 1,2-diferrocenylethane, PhCH<sub>2</sub>OH, and 16.5 percent ferrocenylcarbinol. Furfuryl ferrocenylmethyl ether similarly gave 80 percent methylferrocene, 5 percent diferrocenylethane, and a yellow oil which was free of Fe. Li under THF treated with Me 1-ferrocenylethyl ether similarly gave 63 percent ethylferrocene, 11 percent 2,3-diferrocenylbutane, m. 144-6°, and a red oil which was not identified. Similarly, Me phenyl(ferrocenyl) carbinyl ether gave 51 percent benzylferrocene, m. 74-5°, some 1,2-diphenyl-1,2-diferrocenylethane, m. 264-7°, and a little benzoylferrocene, m. 111-12° (from oxidation of the benzyl analog during handling); this cleavage is best run at -20° once the reaction has started; if run at -5°, the reaction gave but 10 percent benzylferrocene and much red oily material.

1-Ferrocenylethanol in 50 percent MeOH was treated with AcOH at 50°, then cooled slowly to give a red oil, which after treatment with aqueous NaOH, gave 89 percent Me 1-ferrocenylethyl ether,  $b_{0.5}$  96.5-98°, m. 26.5-27.5°. Similarly was prepared 100 percent Me phenyl(ferrocenyl)carbinyl ether, m. 111-112°. Ferrocenylcarbinol shaken 5 min. in Et<sub>2</sub>O-10 percent HCl gave 75 percent bis(ferrocenylmethyl) ether, m. 130-1°, after purification on Al<sub>2</sub>O<sub>3</sub>.

## VI

Rates of cleavage were determined semi-quantitative for [C<sub>5</sub>H<sub>5</sub>FeC<sub>5</sub>H<sub>4</sub>CH<sub>2</sub>NMe<sub>2</sub>R]X, where R = alkyl group and X = Br or I, in 50 percent aqueous dioxane at 100°. The tabulated data indicated that increased size of the R group resulted in increased reaction rate, probably owing to B-strain effects. Ferrocenecarboxanilide was percolated in a Soxhlet extractor with LiAlH<sub>4</sub> in THF 5 hrs. to give 100 percent N-ferrocenylmethylaniline (Ia), m. 84-5°; HCl salt m. 165-7°. Ia in MeCN was treated with MeI 12 hrs. at 0° to give 39 percent N, N-bis(ferrocenylmethyl)aniline (I), m. 164-5°, N-methyl-N-ferrocenylmethylaniline (II), m. 51-2°, and 25 percent N-ferrocenylmethylaniline, m. 84-5°. Similar reaction with MeI in MeOH gave 24 percent I, 40 percent Me ferrocenylcarbinyl ether (III),  $b_3$  118.5-119.5°,  $n_D^{20}$  1.5996, and 21 percent II. II and MeI in PhCH<sub>2</sub>OH 2 days at room temperature gave 53 percent benzyl ferrocenylmethyl ether, m. 88-9°, and some PhNMe<sub>2</sub>. I and MeI in absolute MeOH refluxed 4 hrs. gave 67 percent III. PhCH<sub>2</sub>MgCl and α-dimethylaminoferrocenylacetonitrile 4 hrs. in Et<sub>2</sub>O gave 86 percent (β-phenyl-α-ferrocenylethyl) dimethylamine-HCl, decomposed 154-6°, which with 40 percent NaOH in MeOH gave 87 percent free amine, m. 78-80°, which with MeI in MeCN at 0° overnight gave 84 percent 1-phenyl-2-ferrocenylethene (IV), m. 118-5-119.5° and Me<sub>3</sub>N.HI. Similar reaction in MeOH gave 10 percent IV and 37.3 percent Me β-phenyl-α-ferrocenylethyl ether, m. 54.5-55°. Thus, the N-ferrocenyl substituted anilines failed to yield quaternary salts with MeI and gave only products of decomposition of such salts, formed through ferrocenylalkyl cations. The quaternary salts are unstable, probably owing to existence of F- and B-strain.

435. Rausch, M. D.,  
ORGANOMETALLIC  $\pi$ -COMPLEXES. VII. MERCURIFERRO-  
CENES, Journal of Organic Chemistry, Vol. 28, No. 12,  
1963, pp. 3337-3341 (cf. CA 57, 7303c).

Treatment of 1, 1'-dichloromercuriferrocene with either ethanolic NaI or aqueous  $\text{Na}_2\text{S}_2\text{O}_3$  solution produces  $(\text{C}_{10}\text{H}_8\text{-FeHg})_x$ . The reactions of these materials with either BuLi, followed by carbonation and hydrolysis, or iodine yield ferrocene-1, 1'-dicarboxylic acid and 1, 1'-diiodoferrocene as the major products, respectively, together with lesser amounts monosubstituted ferrocenes and ferrocene. The infrared, nuclear magnetic resonance, and mass spectra of  $(\text{C}_{10}\text{H}_8\text{Fe-Hg})_x$  and of diferrocenylmercury are reported and discussed. The spectral data and chemical reactivity of the new mercuriferrocenes are consistent with the general structural formulation involving units of ferrocene bridged by atoms of mercury in a heteroannular arrangement.

436. Royal Aircraft Establishment, Farnborough, England,  
FERROCENE POLYMERS. PART III. SOME ASPECTS OF  
THE REACTION BETWEEN FERROCENE AND PHENYL-  
SODIUM by W. A. Lee and J. S. Pippett, AD-286 417  
(Unclassified Report).

The reaction of ferrocene with amylsodium and phenylsodium is discussed. Some effects of the method of preparation and purity of the phenylsodium, and of time and temperature variations on the metalation of ferrocene are reported. A reliable procedure for the synthesis of pure 1, 1'-disodioferrocene free from monosodiocompounds was not found; some decomposition of the ferrocene moiety appears to occur during the reaction. The main product from a room-temperature reaction appears to be monosodioferrocene. The mixture of ferrocene and phenylsodium must be stored at room temperature before heating, to avoid very low yields of 1, 1'-disodioferrocene and high yields of by-products. Recommendations for further work are outlined.

37. Ustynyuk, Y. A., Perevalova, E. G., and Nesmeyanov, A. N.,  
REACTIVITY OF COMPOUNDS CONTAINING THE FERRO-  
CENYLMETHYL GROUP. COMMUNICATION 8. WITTIG  
REARRANGEMENT OF FERROCENYLMETHYL ETHERS,  
Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 1.  
January 1964, pp. 70-73.

Refer to item No. 236 for abstract.

## A. Work in United States

439. Aeronautical Systems Division, Nonmetallic Materials Laboratory, Wright-Patterson Air Force Base, Ohio,  
IMPROVED ORGANIC COATINGS FOR TEMPERATURE CONTROL IN A SPACE ENVIRONMENT, FINAL REPORT, 1 AUGUST 1961-31 JULY 1962 by H. H. Hormann, February 1963, Report ASD-TDR-62-917, X63-12045 (Presented at the Society of Aerospace Materials and Process Engineering Meeting, St. Louis, May 6-9, 1962) (Unclassified Report).

Not abstracted.

440. Arizona University, Tucson, Arizona,  
SYNTHESIS OF THERMALLY-STABLE POLYMERS by C. S. Marvel and J. J. Bloomfield, Report No. ASDTDR62 200, AD-275 741, Contract No. AF33 616 7908 (Unclassified Report).

A synthesis was devised which produces pure diacrylylmethane in good yields. Three new soluble polybenzborimidazoles have been prepared by the condensation of 3,3'-diaminobenzidine with the tetrabutyl esters of phenyl-1,3-diboronic acid, phenyl-1,4-diboronic acid and ferrocene-1,1'diboronic acid, respectively. Thermogravimetric analysis curves indicate that the phenyl boronic acids polymers are stable to over 500 C whereas the ferrocene derivative decomposes at about 350 C. Further work was done on the polymerization of 1,3-cyclohexadiene. Improved dehydrogenation procedures were devised for converting poly-1,3-cyclohexadiene linear polyphenyl. Poly2,2'-(m-phenylene-5,5'-bibenzimidazole) was converted to derivatives having cyanomethyl and cyanoethyl groups in place of the imine hydrogen atom.

441. Douglas Aircraft Company Incorporated, Santa Monica, California,  
SYNTHESIS OF FERROCENE-CONTAINING POLYMERS ANNUAL REPORT, MAY 1964-MAY 1965 by E. W. Neuse, K. Koda, E. Quo, and R. K. Crossland, July 1965, Report No. MLTR-65-158, AD-473 383L, Contract No. AF33(615)-639 (Unclassified Report).

This report covers research on the synthesis, identification and characterization of soluble and/or fusible, hydrolytically, thermally and oxidatively stable ferrocene-containing polymeric products of high molecular weight. A polyferrocenylene has been prepared by modified literature procedures.

In addition, Methinyl-bridged and carbonyl-bridged polymers have been synthesized by Lewis acid-catalyzed melt phase and solution condensations of ferrocene with cinnamaldehyde and terephthaloyl chloride, respectively. The soluble products, possessing number-average molecular weights up to 8000 (unsubfractionated), have been identified by chemical and spectroscopic analyses and have been characterized by hydrolysis tests, magnetic measurements and thermogravimetric analyses. Defined low-molecular by-products have been isolated in all instances in support of the structural assignments made.

442. Gill, T. J., III and Mann, L. T., Jr.,  
SYNTHETIC POLYPEPTIDE ANTIGENS. XV. IMMUNOCHEMICAL PROPERTIES OF FERROCENYL-POLYGLU<sup>58</sup>LYS<sup>36</sup>TYR<sup>6</sup> (NO. 2) CONJUGATES, Journal of Immunology, Vol. 96, No. 5, 1966, pp. 906-912 (cf. CA 63, 1537g).

Ferrocenylmethyl isothiocyanate was conjugated with polyGlu<sup>58</sup>Lys<sup>36</sup>Tyr<sup>6</sup> to determine the number of ferrocenyl residues that can be conjugated with a macromolecular without exerting a significant hapten function and to determine how many ferrocenyl residues were necessary to act as antigenic determinants. Two ferrocenyl groups per polypeptide chain slightly enhanced the amount of antibody elicited, but only a small amount of the antibody was directed at the ferrocenyl group; ferrocene was useful as a label for metabolic studies at this level. Larger amounts of ferrocene (10-16 residues per polypeptide chain) showed strong hapten activity with  $\leq 70$  percent of the antibody directed at the ferrocenyl group; ferrocenyl acetic acid inhibited the ferrocene-antiferrocene reaction. The ability of ferrocene to enhance immunogenicity reflected behavior similar to that of aromatic amino acids and cyclohexylalanine. The metallocenes incorporate radioactive heavy metal atoms with relatively long half lives, are biologically stable and probably cannot be reutilized by the animal in any significant amount, and may become electron dense if short polymers of them are attached to the polypeptide chain.

443. Goldberg, S. I. and Matteson, R. L.,  
MULTINUCLEAR FERROCENES. II. SYNTHESIS OF SUBSTITUTED BIFERROCENYLS, Journal of Organic Chemistry, Vol. 29, No. 2, 1964, pp. 323-326 (cf. CA 59, 3950c).

It has been found possible to effect coupling of substituted holoferrocenes by means of treatment with activated copper

bronze to yield substituted biferrocenyls. In addition to coupling products, significant amounts of ferrocene derivatives are obtained which appear to result from formal replacement of halogen by H in the starting material.

444. Melpar Incorporated, Falls Church, Virginia,  
INVESTIGATION OF THE EFFECTS OF IONIZING RADIATION  
ON TRANSITION METAL COMPLEXES OF CYCLOPENTA-  
DIENE, FINAL REPORT, 1 MAY 1964 - 31 MARCH 1965 by  
R. C. McIlhenny and S. A. Honigstein, July 1965, Report  
No. AFMLTR-65-294, AD-476 623, Contract No. AF33(615)-1694  
(Unclassified Report).

Purified monomeric cyclopentadiene was irradiated at various dose rates and total doses. Hydrogen was the only gaseous radiolytic product collected; the yield approximately 0.15 molecule/100 electron volts. Cyclopentene and cyclopentane were also radiolytically produced in trace quantities from highly purified cyclopentadiene. Polycyclopentadiene was formed at liquid nitrogen temperatures with G(-C<sub>5</sub>H<sub>6</sub>) on the order of 110 but varying with dose. Maximum polymer molecular weight exceeded 1,200,000. Ferrocene, purified by sublimation, was irradiated at various dose rates and total doses and was found to be highly stable toward gamma radiation. Hydrogen, cyclopentadiene, cyclopentene, and cyclopentane were found in the volatile fraction with yields of the order of 0.01 molecule/100 electron volts, for both hydrogen and the C<sub>5</sub> group hydrocarbons. A nonsublimable solid fraction was recovered and identified as a mixture of polyferrocenylenes with the cyclopentadiene rings randomly inserted in the polyferrocene chain. The average molecular weight was found to be of the order of 500.

445. Mulvaney, J. E., Bloomfield, J. J., and Marvel, C. S.,  
POLY(BENZBORIMIDAZOLINES), Journal of Polymer Sciences,  
Vol. 62, 1962, pp. 59-72.

Tetra-Bu 1,4-benzenediboronate (I), tetra-Bu 1,3-benzene-diboronate (II), and tetra-Bu 1,1'-ferrocenylenediboronate (III) were condensed with 3,3'-diaminobenzidine to form three poly(benzborimidazolines). Both soluble and melt polymerization techniques were employed. The monomeric model compounds, p-phenylenebis(2-benzborimidazoline), m-phenylenebis(2-benzborimidazoline), and 1,1'-ferrocenylenebis(2-benzborimidazoline) were also prepared. All 3 polymers were soluble in

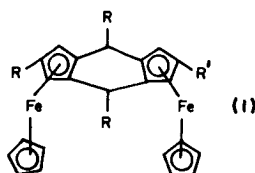


polar solvents such as  $\text{Me}_2\text{SO}$ ,  $\text{HCONMe}_2$ , N-methylpyrrolidone,  $\text{Me}_2\text{NAC}$ , and hexamethylphosphoramide, and had inherent viscosities in the range 0.05-0.35. The polymers were also soluble in  $\text{H}_2\text{SO}_4$ , but hydrolyzed upon precipitation with a large excess of water. A transparent, somewhat brittle, film could be cast from a  $\text{Me}_2\text{NAC}$  solution of the polymer derived from II. This polymer also had adhesive properties. All polymers as well as the model compounds showed a strong, sharp infrared band close to  $3500\text{ cm}^{-1}$ . Polymers derived from I and II were stable up to  $500-600^\circ$ . The polymer derived from III decomposed at  $300-400^\circ$ .

446. Neuse, E. W.,

FERROCENE POLYMERS, U. S. Patent 3,238,185 (cl. 260-80), 1 March 1966, Applied 29 October 1962, 5 pp.

The title polymers probably have the formula I, where R is H, an aryl, alkyl, or alkaryl group, the five-membered rings

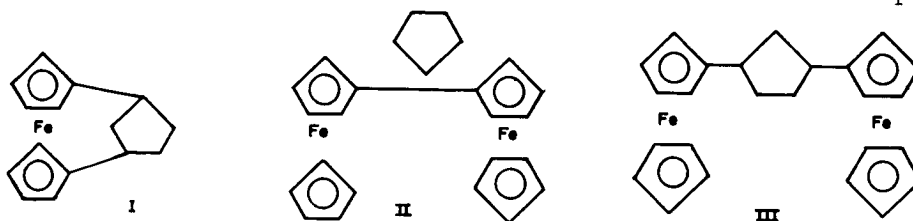


are cyclopentadienyl radicals, and  $\text{R}'$  is a polymer chain of such radicals, terminated by a ferrocenyl group. Of the monomers used, hydroxymethylferrocene (II) is prepared by the method of Lindsay and Hauser (CA 52, 1151b). 1-Hydroxyethylferrocene was made by  $\text{NaBH}_4$  reduction of acetylferrocene in 80:20 dioxane-EtOH solution. These carbinols are polymerized by condensation. Thus, II was ground and melted with 1 percent  $\text{ZnCl}_2$  at  $90^\circ$  in an oil bath under dry N with stirring until an orange-brown crystalline mass formed consisting of bis-(ferrocenylmethyl) ether. The temperature was raised to  $130^\circ$  briefly and was held at  $110^\circ$  for an hr. until the stirrer stalled. The crude polymer was ground cold, washed with MeOH, dried, and dissolved in portions with 60-80 ml. dioxane/10 g. polymer, and reprecipitated by stirring the filtered solution into four times its volume 95 percent aqueous MeOH. A dirty-yellow, powdered solid resulted. This was dissolved in  $\text{C}_6\text{H}_6$  and passed through a chromatographic column packed with activated  $\text{Al}_2\text{O}_3$ . The filtrate was fractionally precipitated from dioxane and dried in vacuo for 1 week, yield 93 percent, partially m.  $130-50^\circ$ , number average molecular weight 3450. This and similar polymers are useful as less volatile substitutes for ferrocene; due to their stability at high temperatures they are useful as scalants, varnishes and

laminating impregnants, and they can be added to A-stage phenolic resins to make useful derivatives. Other Lewis acids can be used to make the polymers, which can also be made by direct polymerization of N,N-dimethylaminomethylferrocene.

447. Neuse, E. W., Crossland, R. K., and Koda, K.,  
 METALLOCENE POLYMERS XIV. METAL-RING BOND  
 CLEAVAGE BY WATER PROMOTED ZINC CHLORIDE,  
Journal of Organic Chemistry, Vol. 31, No. 7, 1966, p. 2409.

Ferrocene-aldehyde water promoted zinc chloride polymerizations in the melt phase gave low yields of polymers (5 to 15 percent yield) which had number average molecular weights of 2000 to 2500. In addition compounds I, II, and III have been isolated and identified. The mechanism of the poly-



merization is discussed as well as the generation of oligomers with  $M_n$  in the 700-1000 range generated on alumina columns from cyclopentenyl ferrocene.

448. Neuse, E. W. and Koda, K.,  
 FERROCENE-CONTAINING POLYMERS. XI. POLYCONDENSA-  
 TION OF FERROCENE WITH O-ANISALDEHYDE, Journal of  
Organometallic Chemistry, Vol. 4, No. 6, 1965, pp. 475-483.

As part of a study on the synthesis of ferrocene-containing polymers with functional side-groups capable of further reaction with crosslinking agents, this paper deals with the polycondensation of ferrocene and o-anisaldehyde. The reactions, catalyzed by  $ZnCl_2$ , are conducted in the melt-phase at the two temperature levels of 135° and 165°. The resulting polymers, isolated in 60-70 percent yield by suitable extraction and precipitation techniques, possess number-average molecular weights up to 4000 (unfractionated). Elemental and spectroscopic analyses, coupled with the isolation and identification of the defined monomeric member, (2-methoxyphenyl)diferrocenylmethane, indicate the polymer backbone to be composed in the expected manner of alternating ferrocenylene and 2-methoxybenzylidene units. Best agreement in elemental composition with this structure is obtained at the 135° level. The 165° level, while leading to higher molecular weights, results in increased formation of repeat units containing two, rather than one,

methoxybenzylidene bridging groups. Irrespective of these minor compositional differences, all polymeric products synthesized are soluble and partially fusible as a consequence of their predominantly linear chain structure. Future work will involve a study of the crosslinking behavior of these products, utilizing the highly nucleophilic character of the methoxy-substituted phenyl side-groups.

449. Neuse, E. W. and Koda, K.,  
POLYCONDENSATION OF N,N-DIMETHYLAMINOMETHYL-  
FERROCENE WITH FERROCENE, Chemical Society of Japan  
Bulletin, Vol. 39, No. 7, 1966, p. 1502.

Not abstracted.

450. Neuse, E. W. and Quo, E.,  
FERROCENE-CONTAINING POLYMERS. INTERMEDIARY  
COMPLEX FORMATION IN THE POLYCONDENSATION OF  
N,N-DIMETHYLAMINOMETHYLFERROCENE, Nature,  
Vol. 204, No. 4970, 1965, p. 494.

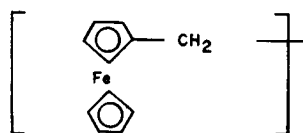
The isolation of  $\text{RCH}_2\text{NMe} \cdot \text{HNMe}_2 \cdot \text{ZnCl}_2 \cdot 2\text{HCl}$  (I) (R = ferrocenyl) as an intermediate in the  $\text{ZnCl}_2$ -HCl-catalyzed polycondensation of N,N-dimethylaminomethylferrocene (II) is described. By using II,  $\text{ZnCl}_2$ , and HCl in the ratio 2:1:2, I is separated in 5-9 percent yield by fractional crystallization from the isotropic-PrOH extract of the reaction mixture. Similarly, equimolecular amounts of II,  $\text{ZnCl}_2$ , and  $\text{H}_2\text{O}$  heated at  $160^\circ$  for 4 hrs. gave I in 8.7 percent yield. The  $\text{H}_2\text{O}$ -soluble complex forms yellow plates, m.  $140-2^\circ$ . In aqueous or alcohol solution, I dissociate reversibly into  $[\text{RCH}_2\text{HNMe}]^+$ ,  $[\text{H}_2\text{NMe}_2]^+$  and  $[\text{ZnCl}_4]^{--}$ . The iridian spectrum of I suggests protonation of the dimethylamine N, while the Mannich base N exist in a nonprotonated form and may involve coordinate covalent  $\text{N} \rightarrow \text{Zn}$  bonding.

451. Neuse, E. W. and Quo, E.,  
POLYCONDENSATION OF FERROCENE WITH FORMALDE-  
HYDE, Chemical Society of Japan Bulletin, Vol. 39, No. 7,  
1966, p. 1508.

Not abstracted.

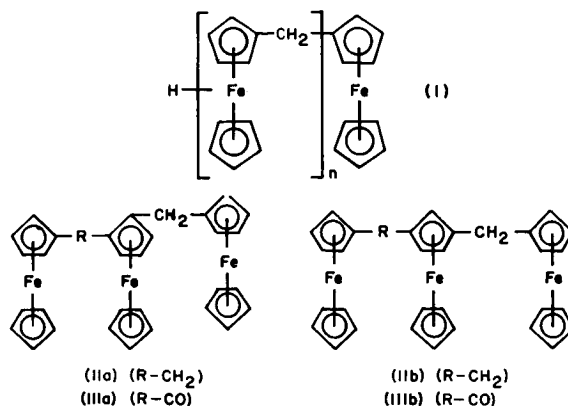
452. Neuse, E. W. and Quo, E. ,  
 THE AUTOCONDENSATION OF N,N-DIMETHYLOMINOMETHYL-  
 FERROCENE, Journal of Polymer Science, Vol. 3A, 1965,  
 p. 1499.

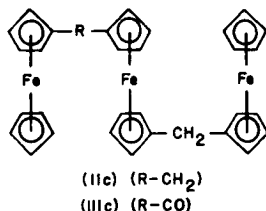
N,N-dimethylaminoferrocene in the presence of a  $\text{ZnCl}_2/\text{HCl}$  catalyst system level to formation of soluble polymers consisting of ferrocenylene units linked by methylene bridges. The crude condensation products prepared in the melt have number average molecular weights of 4000 to 8000. Elemental analysis, infrared spectroscopy and viscometric data, indicate that the polymer has the formula:



453. Neuse, E. W. , Quo, E. and Howells, W. G. ,  
 FERROCENE-CONTAINING POLYMERS. X. ISOMERIC  
 BIS(FERROCENYLMETHYL) FERROCENES, Journal of  
Organic Chemistry, Vol. 30, No. 12, 1965, pp. 4071-4074  
 (cf. CA 63, 8502c).

From a trinuclear fraction of the methylene-bridged ferrocene polymer I, obtained in earlier investigations, the isomeric 1,2-, 1,3-, and 1,1'-bis(ferrocenylmethyl)ferrocenes IIa-c are separated by fractional crystallization in the approximate ratio, 1:5:4. The three isomers are identified by elemental analyses and spectroscopic techniques. Their structural assignments are confirmed by independent synthesis by way of Clemmensen reduction of the corresponding monoketones

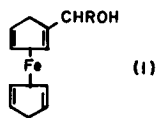




IIIa-c, obtained from ferrocenoyl chloride and diferrocenylmethane under Friedel-Crafts conditions. The established ratio of isomers II, while at best a very crude approximation, corroborates earlier qualitative predictions with regard to the sequence distribution of 1,2-, 1,3-, and 1,1'-substituted recurring units along the backbone of polymer I.

454. Neuse, E. W. and Trifar, D. S.,  
POLYCONDENSATION OF FERROCENYL CARBINOLS AND  
SUBSTITUTION ORIENTATION EFFECTS, American Chemical  
Society Journal, Vol. 85, No. 13, 1963, pp. 1952-1958.

Based on previous studies on the reaction of ferrocene with representative  $\alpha$ -arylcarbinols, self-condensation reactions of three ferrocenylcarbinols, hydroxymethylferrocene, (1-hydroxyethyl)ferrocene and  $\alpha$ -hydroxybenzylferrocene (I, R = H, Me, Ph, respectively), resulting in the formation of -CH(R)-linked ferrocenylene polymers are described. The acid-catalyzed reactions are conducted in the melt phase and lead to crude reaction products in the  $M_n$  range 1000-6000. The polymers are soluble in a number of organic solvents, and the lower members show a defined melting range. Quantitative infrared spectroscopic analysis has been applied to elucidate structural correlations and the effect of variables on the ring substitution orientations occurring under these conditions of polymer formation compared to the general behavior of the ferrocene nucleus under usual nonpolymeric conditions.



455. Plastics Laboratory, Princeton University, New Jersey,  
HIGH POLYMER RESEARCH by L. F. Rahm, AD-239 173  
(Unclassified Report).

Not abstracted.

456. Plastics Laboratory, Princeton University, New Jersey,  
HIGH POLYMER RESEARCH by L. F. Rahm, AD-253 073  
(Unclassified Report).

This report contains a Chemical Section; Ziegler polymerization of nonconjugated double bond systems, directional hydrogen bonding-property relationships in polyamides, ferrocene chemistry, intramolecular pi-hydrogen bonding.

Dielectrics Section; Semiconduction in high polymers, melt behavior of sheared high polymers, and stereoregularity and dielectric behavior of high polymers. Mechanical Section; Dynamic mechanical properties of polyethylenes, dynamic mechanical properties of polybutene, polymer melt elasticity, elastic melt extrusion, cold working of polycrystalline polymers, and low temperature properties of polypropylene.

457. Plastics Laboratory, Princeton University, New Jersey,  
HIGH POLYMER RESEARCH by L. F. Rahm, AD-284 382  
(Unclassified Report).

This report contains a Chemical Section; Polymerization of nonconjugated double bond systems, synthesis of multiple-strand polymers, ferrocene chemistry. Dielectrics Section; Semiconduction in high polymers. Mechanical Section; Phase transitions in polypropylene, phase transitions in polybutene-1, deformation characteristics of spherulites, failure mechanism in glassy state polymers, flow behavior in polymer melts.

458. Plastics Laboratory, Princeton University, New Jersey,  
SYNTHESIS AND CHARACTERIZATION OF SOME HIGHLY  
CONJUGATED SEMI-CONDUCTING POLYMERS by E. H.  
Engelhardt and H. A. Pohl, AD-273 723 (Unclassified Report).

A series of highly conjugated, semiconducting polymers was synthesized and electronically characterized.

The conductivities of polymers, produced, ranged from approximately one-tenth to the third power to tenth to the eleventh power MHO cm at room temperature. A correlation between conductivity in PAQR polymers, and the size of the aromatic hydrocarbon monomer, were established. Thermoelectric power measurements, and a Hall determination generally indicated p-type conductivity in the polymers. Additional electrical determinations included: Thermal activation energy of conduction, ohmic behavior, carrier species, electron spin density, thermal and chemical stability, and photo-electrical effects.

The electronic nature of conduction in the polyacene quinone radical polymers was proven by observing a large (positive) Hall coefficient, and the stability of conduction to large charge passage. Nonohmic behavior was observed at low electric field strengths.

459. Plastics Laboratory, Princeton University, New Jersey, TITLES NOT AVAILABLE by L. F. Rahm, D. S. Trifan, and H. A. Pohl, AD-230 916; 1 June 1961, Report No. QR 61, AD-260 185; 1 November 1960, Report No. QR 59, AD-248 981; 1 December 1961, Report No. QR 63, AD-270 961; 1 August 1960, Report No. QR 58, AD-243 943; 16 July 1962, Final Report No. 65 (Unclassified Report).

A series of reports consisting of the fundamental work on ferrocene polymers is described in the areas of dielectrics, elasticity, electrical conductance, mechanical properties, molecular structure, semi-conductors. The work is of broad scope.

460. Rosenberg, H. and Neuse, E. W., FERROCENE-CONTAINING POLYMERS A REINVESTIGATION OF THE POLYRECOMBINATION OF FERROCENE, Journal of Organometallic Chemistry, Vol. 6, 1966, pp. 76-85.

Earlier work by Korshak and other Russian authors on the preparation of polyferrocenylenes by the recombination reaction of ferrocene in the presence of tert-butyl peroxide has been reinvestigated. It has been demonstrated that, under carefully controlled conditions at temperatures near 200°, ferrocene can indeed be polymerized to give soluble polymeric compounds, comparable in molecular weight range and physical properties with Korshak's products. These polymers, however, possess overall elemental compositions distinctly differing from that of polyferrocenylene. Spectroscopic and elemental analyses, corroborated by the isolation not only of biferrocenyl and terferrocenylys, but also of diferrocenylmethane and ferrocenylmethyl tert-butyl ether as by-products, indicate the polymer chains to be composed of small polyferrocenylene segments interlinked by methylene and aliphatic ether groups. These bridging groupings are believed to have arisen through the involvement of methyl and tert-butyl radicals generated by thermal decomposition of the tert-butyl peroxide, with methylferrocene postulated as an additional intermediate. Consistent with the presence of such non-ferrocene constituents, the

polymers exhibit poor hydrolytic stability and, in thermogravimetric analysis, show a thermal stability behavior inferior to that expected for a polymeric compound strictly composed of ferrocenylene units.

461. Spilners, I. J. and Pellegrini, J. P, Jr.,  
SYNTHESIS OF POLYFERROCENYLENE, Journal of Organic Chemistry, Vol. 30, No. 11, 1965, pp. 3800-3804.

Polyferrocenylene was formed when cobaltous chloride or an organic halide was added to lithiated ferrocene. The direct bonding of ferrocene nuclei in the polymerization reactions is accounted for by coupling of ferrocenyl radicals. Identification of ferrocene derivatives by low and high voltage mass spectrometry is demonstrated.

462. Texas Instruments Incorporated, Dallas, Texas,  
ORGANIC MATERIALS FOR ELECTRONIC APPLICATIONS,  
QUARTERLY PROGRESS REPORT, Author Unknown, October 1964, Report No. TI-08-64-161, AD-460 929, Contract No. AF33(615)-1364 (Unclassified Report).

Organic thin film polymers have been evaluated and found unsuitable as possible dielectric materials on the silicon adaptive logic elements. Evaluation of the polymers as capacitor dielectrics has been extended to 2.5 gc by measuring capacitance as a function of frequency. The polymers perform satisfactorily in capacitors but fail when used in a thin film-integrated circuit hybrid because of the high processing temperatures required for other steps in the production. Organic polymer films have also been deposited as insulation over thin metal films used as magnetic memory planes, but the evaluation is incomplete. The polymer adheres well to the metal and appears to be pinhole free when tested with a mercury globule. However, evaporated gold stripes showed a high frequency of shorts to the base metal. Several new compounds have been included. Preparation of longer chain metal organic polymers in a melt has been considered. Polymercuriferrocene and polyaminoquinone (PAQ) polymers were prepared and evaluated.



NEW COMPOUNDS AND POLYMERS CONTAINING SILICON  
AND FERROCENE LINKED THROUGH CARBON BRIDGES,  
University Microfilms (Ann Arbor Michigan), Order No. 64-5995,  
145 pp., Dissertation Abstract, Vol. 25, No. 1, 1964,  
pp. 114-115.

The preparation of new materials containing silicon and ferrocene linked through carbon bridges was investigated. Twenty one compounds and polymers are reported.

Attempts to acylate ferrocene with  $\beta$ -trimethylsilylpropionyl chloride as a conventional complex with aluminum chloride failed due to decomposition of the acid chloride. Detailed studies showed that the decomposition products consisted predominantly of chlorotrimethylsilane, ethylene and carbon monoxide. By the slow addition of aluminum chloride powder to a solution containing both the acid chloride and ferrocene, this decomposition was circumvented in that normal acylation then occurred to give the ketone,  $\beta$ -trimethylsilylpropionylferrocene, in good yield. These findings are interpreted in simple ionic terms. The acid chloride first reacts with aluminum chloride in a normal fashion to give an acylonium ion which, however, can then take either of two reaction courses: elimination or acylation. The presence of a suitable substrate which can react with the acylonium ion as it is formed favors the latter course

The monoketone,  $\beta$ -trimethylsilylpropionylferrocene, was found to undergo cleavage of one methyl group from silicon by reaction with concentrated sulfuric acid, methane being liberated. Subsequent hydrolysis of the reaction mixture gave the symmetrical disiloxane derivative. Similarly, the heteroannular diketone analog gave the linear polymeric disilozane derivative. The same pattern of synthesis was more directly achieved by acylating ferrocene with an  $\omega$ -chlorosilyl acid chloride, after which the usual hydrolysis step also served to hydrolyze the chlorine-silicon bond. The presence of the chlorine atom bonded to silicon was found not to interfere with the acylation reaction.

In a similar fashion, monoacylation of ferrocene with an  $\omega$ -dichlorosilyl acid chloride followed by hydrolysis gave a silicone homopolymer containing the ferrocene nucleus in a pendant position. The addition of dichlorodimethylsilane after the acylation step followed by hydrolysis of the mixture resulted in the formation of silicone copolymers.

Ketone type materials were reduced, before and after conversion to disiloxane derivatives, to corresponding alkane type

materials. Alkane type materials were converted to disiloxane derivatives, including polymeric disiloxanes, by utilizing the cleavage of one methyl group from silicon by concentrated sulfuric acid.

Aluminum chloride, presumably through its hydrogen halide complex, was found to effect the same cleavage of one methyl group from an  $\omega$ -trimethylsilyl grouping as was effected by concentrated sulfuric acid. However, with aluminum chloride such cleavage occurred only as a minor side reaction.

464. Wilkus, E. V. and Berger, A.,  
METALLOCENE ORGANOPOLYSILOXANES, COMPAGNIC  
FRANCAISE THOMSON-HOUSTON, French Patent 1,396,274  
(cl. C 07f), 16 April 1965, Applied 27 May 1964, 11 pp.

Compounds of the general formula  $[(C_5H_5)M(C_5H_4)(CO)_m(CH_2)_nSiMe_2]_2O$  (I) are prepared. Thus, 4 parts  $Mc_3SiCH_2CH_2COCl$  in  $CH_2Cl_2$  is mixed with 4.52 parts  $[C_5H_5]Fe[C_5H_5]$  in  $CH_2Cl_2$ , 3.4 parts  $AlCl_3$  is added in ~80 min., and the mixture hydrolyzed with 50 parts cold  $H_2O$  and 7 parts  $HCl$  to give  $Me_3SiCH_2CH_2CO[C_5H_4]Fe[C_5H_5]$  (II). A mixture of 0.5 parts II and 18 parts concentrated  $H_2SO_4$  is agitated 30 min., the mixture added to 35 parts cold  $H_2O$ , the whole kept 20 hrs. and extracted with  $CH_2Cl_2$ , and the  $CH_2Cl_2$  evaporated to give 76 percent 1,3-bis( $\beta$ -ferrocenylethyl)tetramethyldisiloxane, m.  $136-7^\circ$ . Similarly prepared are the following I (M, m, and n given): Os, 1, 2; Fe, 0, 3. Powder  $AlCl_3$  (6.8 parts) is added to a mixture of 9.04 parts  $Fe[C_5H_5]_2$  and 9.96 parts  $MeSiCl_2CH_2CH_2COCl$  in 133 parts  $CH_2Cl_2$ , the mixture is agitated 24 hrs., 2.4 parts  $AlCl_3$  added, a mixture of 150 parts cold  $H_2O$  and 20 parts concentrated  $HCl$  added, then 200 parts  $CH_2Cl_2$ , and the mixture kept several days to give a polymethyl ( $\beta$ -ferrocenylethyl)siloxane, containing the unit:  $[C_5H_5]Fe[C_5H_4]-COCH_2CH_2SiMeO$  and containing silanol end-groups, which can be used as a ultraviolet rays absorber.

65. Wyandotte Chemicals Corporation, Michigan,  
INTERMEDIATES FOR HIGH-TEMPERATURE STABLE POLY-  
MERS by P. Szecsi, J. D. Behun, P. T. Kan, and R. A. Moore,  
January 1964, Report No. TDR 649, AD-439 847, Contract  
No. AF33(657)-10819 (Unclassified Report).

Synthetic methods and experimental procedures employed in the preparation of specified intermediates for high-temperature stable polymers are described.

In some cases known procedures were modified in order to facilitate large-scale laboratory preparations. In a few instances, where procedures were not available, some exploratory effort was expended to develop preparative methods. The following compounds were synthesized in a high state of purity by published and/or adapted procedures: 2,4-diphenyl-6-chloros-triazine; 2,4-diboromo-6-phenyl-s-triazine; diferrocenylketone; diferrocenylmercury; 1,1'-diiodoferrocene; ferrocene mono-boronic acid; poly-m-phenoxylenes; dichlorodiphenylgermainum; 2-hydroxyisophthalic acid. Trifluoropyrimidine and triphenyl-aluminum were procured directly.

466. Wyandotte Chemicals Corporation, Michigan,  
INTERMEDIATES FOR HIGH TEMPERATURE STABLE POLY-  
MERS, FINAL REPORT 1 JANUARY 1964 - 13 DECEMBER  
1964 by P. Szecsi, February 1965, Report No. AFML-TR-  
65-46, AD-464 487, X65-18302, AF Material Laboratory,  
Wright-Patterson Air Force Base, Ohio, Contract No.  
AF33(657)-10819 (Unclassified Report).

The synthetic methods and experimental procedures adopted for the preparation of materials specified by RTD that are to be used as intermediates in high-temperature polymer studies, are discussed. The compounds synthesized include ferrocenes, aromatic nitro and amino compounds, o-phenylenediamine derivatives, benzothiadiazole, a halotriazine, polyesters and a number of polyfluoroaromatic compounds.

467. Wyandotte Chemicals Corporation, Michigan, INTERMEDIATES FOR HIGH-TEMPERATURE STABLE POLYMERS, TECHNICAL DOCUMENTARY REPORT, 1 JANUARY 1962 - 31 DECEMBER 1962 by P. Szecsi, J. D. Behun, R. L. Schaaf, and K. K. Aoki, January 1963, Report No. ASD-TDR-63-130, X63-15878, Directorate of Material and Processes, Wright-Patterson Air Force Base, Ohio, Contract No. AF33(657)-7613 (Unclassified Report).

The synthetic methods and experimental procedures adopted for the preparation of materials specified by ASD that are to be used as intermediates in high-temperature polymer studies, are discussed. The compounds include ferrocenes,  $\alpha,\omega$ -diolefins, and triazine derivatives.

#### B. Russian Effort

468. Belov, V. F., Vishnyakova, T. P., Gol'danskii, V. I., Makarov, E. F., Paushkin, Y. M., Sakolinskaya, T. A., Stukan, R. A., and Trukhtanov, V. A., INVESTIGATION OF FERROCENE COPOLYMERS BY MEANS OF THE MOESSBAUER EFFECT, Doklady Akademii Nauk SSSR, Vol. 159, No. 4, 1964, pp. 831-834 (In Russian).

Polyferrocene, poly(vinylferrocene), and the copolymers of ferrocene with the following compounds were studied:  $\text{Me}_2\text{CO}$ , naphthalene,  $\alpha$ -bromonaphthalene,  $p\text{-Cl}_2\text{C}_6\text{H}_4$ , salicylaldehyde,  $\text{BzH}$ , and phthalic anhydride. The Moessbauer velocity spectra for the  $\text{C}_6\text{H}_6$ -soluble portions of the polymers all exhibit a doublet structure, with a quadrupole splitting between 2.2 and 2.4 mm./sec. and a chemical shift of 0.40-0.55 mm./sec. relative to Fe in a stainless-steel reference standard. The data support the hypothesis of a linear structure for these  $\text{C}_6\text{H}_6$ -soluble portions. For the  $\text{C}_6\text{H}_6$ -insoluble fractions, the quadrupole splitting is lower. Furthermore, at liquid N temperatures, 2 doublets occur. One corresponds to 3-dimensionally linked polymer units, in which Fe atoms form part of a conjugated system. The other corresponds to the linear chains in the polymer. At room temperature, only the former is observed. The relative proportions of each type of linkage can be determined.

469. Berlin, A. A. and Kostroma, T. V.,  
POLYMERS WITH CONJUGATED BONDS AND HETEROATOMS  
IN A CONJUGATED CHAIN (Foreight title not available),  
Translated into English from Russian by the Foreign Technology  
Division, Air Force Systems Command, Wright-Patterson Air  
Force Base, Ohio, Report No. FTD-TT-64-1261/1+2, AD-615  
243, N65-28844, 26 April 1965 (Geterotsepnye Vysokomol-  
ekularnye Soyedineniya Sb. Statey).

Salicyl derivatives of ferrocene were obtained that were never described before. Polymer chelate complexes were obtained for tetrasalicylates of ferrocene with copper, beryllium, bi- and tetravalent iron, aluminum and magnesium, and complex compounds and disalicyl ferrocene with silver and copper. The thermal stability of the complexes obtained was determined and it was shown that the greatest resistance to heat is possessed by complexes with beryllium, as well as with Mg and Al, which stand heating up to 200 C without significant loss in weight. The least thermal stability was observed in the case of complexes with copper, which at 200 C in the course of 5 minutes, lose 30 percent of their weight. It was established that the complexes of salicylates of ferrocene. In contrast to the corresponding monomer products, possess considerably higher magnetic susceptibility and higher electrical conductivity.

470. Berlin, A. A. and Kostroma, T. V.,  
POLYMERS WITH CONJUGATED BONDS AND HETEROATOMS  
IN THE CONJUGATE CHAIN. XXXVI. POLYMERIC CHELATE  
COMPOUNDS OF SALICYL DERIVATIVES OF FERROCENE,  
Vysokomolekul. Soedin., Geterotsepnye Vysokomolekul.  
Soedin., 1964, pp. 53-58 (CA 61,5797c).

Ferrocene (I) (33.5 g.) in 68 ml.  $H_2SO_4$  was added to ice water. To the solution at room temperature, a solution of a diazonium salt of 91.8 g. p-aminosalicylic acid was added. The precipitate formed on standing was dissolved in 10 percent KOH and 5.31 g. I removed by filtration. The  $C_6H_6$  extraction of the precipitate formed after acidification yielded 1.62 g. of a mixture of mono-, di-, and trisubstituted I. Extraction of the residue with dioxane yielded 37.4 g. tetrasalicylferrocene (II) and a residue of 1.2 g. of pentasalicylferrocene. Ag salts of II and disalicylferrocene were prepared, as were complexes with Cu, Be,  $Fe^{++}$ ,  $Fe^{+++}$ , Al, and Mg.

471. Dulov, A. A., Slinkin, A. A., and Rubinshtein, A. M.,  
ELECTRIC AND MAGNETIC PROPERTIES OF THERMALLY  
TREATED FERROCENE BASE POLYMERS (Foreign title not  
available), Translated into English from Russian by the Foreign  
Technology Division, Air Force Systems Command, Wright-  
Patterson Air Force Base, Ohio, Report No. FTD-TT-64-1365,  
AD-609 782, January 1965 (Vysokomlekulyarnye Soedineniya).

It was shown that the semiconductor properties of ferrocene base polymers are determined not only by the degree of conjugation along the individual polymeric chain, but mainly by the nature of packing and interaction of macromolecules in the polymer.

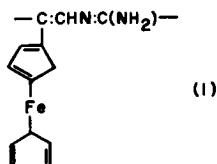
The data obtained are in conformity with the assumption that the noticeable ferromagnetism of ferrocene polymers, which have been pressed and heated in vacuum, one cannot completely exclude the possibility of thermal decomposition of the polymer with the formation of ordinary ferromagnetic iron compounds.

472. Dulov, A. A., Slinkin, A. A., and Rubinshtein, A. M.,  
ELECTRIC AND MAGNETIC PROPERTIES OF THERMALLY  
TREATED FERROCENE BASE POLYMERS (Foreign title not  
available), Translated into English from Russian by the Foreign  
Technology Division, Air Force Systems Command, Wright-  
Patterson Air Force Base, Ohio, Report No. FTD-TT-64-  
1365/1+2, AD-609 782, N65-17089, 6 January 1965 (Vysokomol.  
Soedineniya).

Polyamides were prepared from the cis- and trans-isomers of 4-aminocyclohexylacetic acid. Those from the cis-isomers are soluble in phenol, cresols, concentrate sulfuric acid, hydrochloric, formic, trifluoroacetic acids and other solvents of polyamides, whereas those from the trans-monomers dissolve only in concentrated sulfuric acid and do not soften up to a temperature of 498° to 516° above which they undergo degradation. No interconversion of cis- and trans-forms on polycondensation is observed. High melting, isomorphously substituted copolyamides were obtained by copolycondensation of trans-4-aminocyclohexylacetic acid with  $\epsilon$ -caprolactam.

73. Golubeva, I. A. and Vishnyakova, T. P.,  
HETEROPOLYCONDENSATION OF ACETYLFERROCENE WITH  
UREA, *Plasticheskie Massy*, No. 12, 1965, pp. 10-12 (In  
Russian).

The introduction of ferrocene into polymers with a conjugated bond system and with heteroatoms in the conjugated chain imparts specific electrical and magnetic behavior to the polymers. A polymer containing units of structure I was prepared by heteropolycondensation of acetylferrocene (II) with urea. The reaction was carried out in a metal autoclave, with



melted  $\text{ZnCl}_2$  as a catalyst and in the absence of atmosphere, O, the residual II was extracted by ether. Two polymer fractions were obtained. The fraction extracted with  $\text{C}_6\text{H}_6$  was precipitated by MeOH. The polymer fraction soluble in  $\text{C}_6\text{H}_6$  was washed with 10 percent HCl and then  $\text{H}_2\text{O}$  until no  $\text{Cl}^-$  was present in the filtrates. The polymers obtained were dried to constant weight in vacuo at  $40-50^\circ$ . The reaction was studied under various conditions: temperature range  $110-90^\circ$ ; II/urea/ $\text{ZnCl}_2$  ratio 1:1:2 to 1:1:0.36; reaction time 3, 5, and 8 hrs. The optimum ratio was 1:1:0.72 and gave a 54.8 percent yield. The polymer yield decreased with decreasing temperature. The maximum yield (56.4 percent) was obtained in 8 hrs at  $150^\circ$  and the optimum ratio of parent compounds. The polymer fractions are dark, infusible powders. The  $\text{C}_6\text{H}_6$ -soluble fraction decomposed at  $350^\circ$ . Its molecular weight is  $\sim 1000$ . The structure of the polymer was determined by infrared analysis. The calculated elementary composition of a monomer unit was C 61.95, H 4.75, N 11.1, Fe 22.2 percent. Terminal groups were not considered. The experimental values were C 62.34, H 5.42, N 5.97, Fe 20.72 percent. The low value of N is due to the method used. When the chain is longer and terminal groups are taken into account, calculated values agree well with the experimental. The infrared spectra of the polymer show characteristic absorption bands for C:N, C:C, and  $\text{CNH}_2$  bond vibrations. The presence of amino groups was proved also by potentiometric titrn. Nuclear magnetic resonance studies confirmed the presence of conjugated double bonds. The effect of temperature on the electrical conditions of the

polymer was studied at 20-300° and  $5 \times 10^{-4}$  mm. The condition versus temperature plot gave an exponential curve. Specific conditions of the polymer is  $4.7 \times 10^{-7}$  ohm<sup>-1</sup>-cm<sup>-1</sup>.

474. Karimov, Y. S. and Shchegolev, I. F.,  
MAGNETIC PROPERTIES OF FERROCENE POLYMERS,  
Doklady Akademii Nauk SSSR, Vol. 146, 1962, pp. 1370-1371  
(cf. Nesmeyanov, et al., CA 55, 21081i, 17147d).

Poly (ethanoferrocene) with molecular weight 100 C, after careful purification from possible magnetic impurities, was diamagnetic and has a specific susceptibility of  $-0.75 \times 10^{-6}$ . Monomeric ferrocene has a value of  $-0.55 \times 10^{-6}$ . The polymer remains diamagnetic at 77°K, and only at liquid-He temperature does it become slightly paramagnetic. Almost total absence of paramagnetism was also found in a specimen of linear polyferrocenylene; at room temperature it was diamagnetic with a specific susceptibility of  $-0.5 \times 10^{-6}$  and was somewhat paramagnetic only in liquid He. The previously reported magnetism of these polymers was caused by magnetic impurities.

475. Korshak, V. V., Sosin, S. L., and Chistyakova, M. V.,  
THE USE OF POLYRECOMBINATION REACTION IN PREPARATION OF POLYMERS, Doklady Akademii Nauk SSSR, Vol. 121, 1958, pp. 299-302.

Heating p-C<sub>6</sub>H<sub>4</sub>(CHMe<sub>2</sub>)<sub>2</sub> at 170-200° with gradual addition of (Me<sub>3</sub>CO)<sub>2</sub> gave a polymer which contains varying amounts of insoluble fraction. The product, m. 210-30°, is mainly amorphous (10 percent crystallinity by X-ray pattern). The insoluble portion, decomposes 300°, is 60 percent crystalline. Increased concentration of peroxide results in increased molecular weight of the polymer. The typical radical mechanism of chain formation is discussed at length. Bz<sub>2</sub>O<sub>2</sub> failed to give any insoluble products, since the BzO radicals being less active do not attack the H atoms of the Me groups. Addition of BzOH to the original reaction mixture also has the same effect. This reaction also gave polymers from Ph<sub>2</sub>, p-xylene, iso-Pr<sub>2</sub>CO, diisopropylferrocene, and p-C<sub>6</sub>H<sub>4</sub>Cl<sub>2</sub>.



476. Paushkin, Y. M., Polak, L. S., Vishnyakova, T. P., Patalakh, I. I., and Machus, F. F.,  
 NEW IRON-CONTAINING POLYMERS ON THE BASIS OF  
 FERROCENE AND THEIR ELECTROPHYSICAL PROPERTIES  
 (Foreign title not available), Translated into English from  
 Russian by the Foreign Technology Division, Air Force Systems  
 Command, Wright-Patterson Air Force Base, Ohio, Report  
 No. FTD-TT-64-773/1+2, AD-608 051, N65-13011, 19 October  
 1964 (Vysokomol Soedineniya).

On the basis of ferrocene and its derivatives 14 new polymers were obtained by polyrecombinations and condensation polymerizations. The polymers represent polyconjugative systems and possess electrical resistances from  $1 \cdot 10^{12}$  to  $1 \cdot 10^9$  cm · ohm and activation energy from 0.3 to 1.74 eV. An energy transfer from the valence zone into the conductivity zone of the macromolecules of the polymer of 1,1'-diacetylferrocene was obtained through the excitation of the  $\pi$ -electrons. This took place, basically, by surface adsorption.

477. Paushkin, Y. M., Vishnyakova, T. P., Sokolinskaya, T. A., Patalakh, I. I., Machus, F. F., and Kurasheva, I. D.,  
 NEW IRON-CONTAINING MONOMERS AND POLYMERS FROM  
 FIVE-MEMBERED CYCLIC NAPHTHENES, Tr. Mosk. Inst. Neftekhim. i Gaz. Prom. Vol. 44, 1963, pp. 15-26.

Ferrocene (I) heated 5 hrs. at 60° with an olefin (II) and 25 percent  $H_3PO_4 \cdot BF_3$  gives the following yields of alkylferrocenes (II, weight-percent conversion of I, and weight-percent of mono-, di-, and polyalkylferrocenes in the product shown): iso-Bu, 86.6, 55.7, 38.0, 6.3; isoamyl, 70, 57.5, 40, 2.5; isootyl, 65, 83, 17, --. Values for alkylation with isobutylene with  $AlCl_3$  under the same conditions are 83.5, 27.7, 37.5, and 34.8, respectively. For the products, b.p./mm.  $n_D^{20}$ , and  $d_{20}$  are given:  $C_5H_5FeC_5H_4Bu$ -iso, 103-4°/4, 1.5730, 1.1852;  $C_5H_5FeC_5H_3(Bu$ -iso) $_2$ , 124-8°/3, 1.5563, 1.1192;  $C_5H_5FeC_5H_4(C_5H_{11}$ -iso) $_2$ , 135-40°/4, 1.5755, 1.1681;  $C_5H_5FeC_5H_3(C_5H_{11}$ -iso) $_2$ , 162-7°/4, 1.5609, 1.1253;  $C_5H_5FeC_5H_4(C_8H_{17}$ -iso), 155-60°/3, 1.5626, 1.1205;  $C_5H_5FeC_5H_8(C_8H_{17}$ -iso) $_2$ , 230-5°/3, 1.5558, 1.0824. Alkylferrocenes heated at 200° with  $(tert-BuO)_2O_2$  give polymers, m. 285-300°, with molecular weights of 1200-2280. I heated similarly with  $(tert-BuO)_2O$  and  $p-Cl_2C_6H_4$ ,  $Ph_2$ ,  $\alpha$ -bromonaphthalene, or quinoline gives a mixture of soluble and insoluble polymers, some not m. up to 500°, showing electron spin

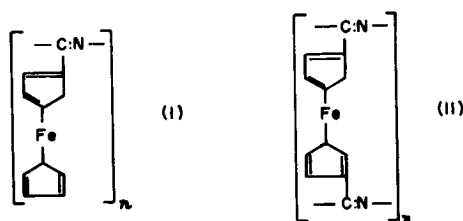
resonance signals and semiconducting properties (positive temperature coefficient of electrical conductivity). Acetylferrocene heated 20 hrs at 200° with  $\text{ZnCl}_2$  gives 90 percent  $+\text{CH}:\text{C}(\text{C}_5\text{H}_4\text{FeC}_5\text{H}_5)+\text{n}$ , mostly insoluble and unchanged by heating to 500°, and also having semiconducting properties.

478. Royal Aircraft Establishment, Farnborough, England,  
 THE SYNTHESIS AND CERTAIN MAGNETIC PROPERTIES OF  
 THE POLYFERROCENES by A. N. Nesmeyanov, V. V. Korshak,  
 and V. V. Voevodskii, AD-264 048 (Unclassified Report).

The synthesis of polyferrocenylenes, polydiisopropylferrocenes, polymethylene and polyethyleneferrocenes is described. Some of their properties, in particular magnetic characteristics, are also described.

479. Vishnyakova, T. P., Golubeva, I. A., and Paushkin, Y. M.,  
 SYNTHESIS OF NITROGEN-CONTAINING FERROCENE  
 POLYMERS WITH CONJUGATED BONDS, Vysoknmolekul  
Soedin, Vol. 8, No. 1, 1966, pp. 181-185 (In Russian) (CA 61,  
 13432d).

New N-containing ferrocene polymers with conjugated double bonds, i. e. poly(ferrocene nitriles) (I and II), were prepared from amides and  $\text{NH}_4$  salts of ferrocenecarboxylic acids and also directly from ferrocene and  $\text{H}_2\text{NCOCl}-\text{ZnCl}_2$



complexes. The dependence of the polymer yield on temperature, reaction time, and ratio of reagents was studied. All polymers showed a narrow 1-component signal in the E. S. R. spectrum with concentration  $10^{17} - 10^{20}$  spins/g. The electroconductivity depended exponentially on temperature and was  $10^{-8} - 10^{-14} \text{ ohm}^{-1} \text{ cm}^{-1}$  at 50°.

C. Other Nations

480. Greber, G. and Hallensleben, M. L.,  
SYNTHESIS OF BIFUNCTIONAL ORGANOSILICON DERIVATIVES  
OF FERROCENE AND THEIR POLYMERIZATION, Makromolec-  
ular Chemistry, Vol. 92, 1966, pp. 137-148.

The addition of 1,1'-bis-(dimethylhydrosilyl)-ferrocene to C-C-unsaturated compounds containing functional groups in presence of  $H_2PtCl_6$  as catalyst results in compounds with two functional groups R, i.e. dicarboxylic acids, diesters, diols, diamines, and diepoxides. These ferrocene compounds react with suitable partners to form polymers containing 1,1'-bis-(dimethylsilyl)-ferrocene segments whose thermostability is examined.

481. Greber, G. and Hallensleben, M. L.,  
SYNTHESIS AND POLYMERIZATION OF BIFUNCTIONAL  
ORGANOSILICON FERROCENE DERIVATIVES, Makromolekular  
Chemie, Vol. 92, 1966, pp. 137-148 (In German) (cf. CA 63,  
16479c).

Refer to Item No. 304 for abstract.

482. Hata, K., Motoyama, I., and Watanabe, H.,  
THE DIRECT FORMATION OF BIFERROCENYL AND POLY-  
FERROCENYLS FROM FERROCENYLLITHIUM, Chemical  
Society of Japan Bulletin, Vol. 37, 1964, p. 1719.

Although many synthetic methods of biferrocenyl have been proposed, all of these routes are circuitous and troublesome. Moreover, the formation of polyferrocenyls other than biferrocenyl has never been reported. The present authors wish to report on the direct formation of biferrocenyl and polyferrocenyls from ferrocenyllithium.

483. Okawara, M., Takemoto, Y., Kitaoka, H., Haruki, E., and Imoto, E.,

SYNTHESES AND REACTIONS OF FUNCTIONAL HIGH-MOLECULAR-WEIGHT COMPOUNDS. X. SYNTHESIS OF 1, 1'-DISUBSTITUTED FERROCENES AND THEIR ADDITION OR CONDENSATION POLYMERIZATION, Kogyo Kagaku Zasshi, Vol. 65, 1962, pp. 685-688.

Compounds synthesized were ferrocene (I), 1, 1'-diacetylferrocene (II), 1, 1'-bis(1-hydroxyethyl)ferrocene (III), 1, 1'-ferrocenedicarboxylic acid (IV), di-Me 1, 1'-ferrocenedicarboxylate (V), 1, 1'-bis(hydroxymethyl)ferrocene (VI), 1, 1'-ferrocenedicarboxylic acid dichloride (VII), 1, 1'-ferrocenedicarboxylic acid diazide (VIII), and 1, 1'-ferrocene diisocyanate (IX). I, m. 172-3°, was prepared in 76 percent yield by the reaction of cyclopentadiene with  $\text{FeCl}_2$  by using  $\text{Et}_2\text{NH}$  or  $\text{EtONa}$  as the catalyst. II, m. 130-1°, was obtained in 50 percent yield by the acetylation of I with  $\text{AcCl}$ . III, m. 69-71°, was prepared in 80 percent yield by reducing II with  $\text{LiAlH}_4$  under N atmosphere IV, decomposes 242-7°, was obtained in 36.5 percent yield by treating with  $\text{Na}_2\text{CO}_3$  aqueous solution a I-Na dispersion which was prepared by the reaction of I with PhNa dispersion. V, m. 112-14°, was obtained in 72 percent yield by esterifying IV with MeOH. VI, m. 108.5-9.5°, was obtained in 56 or 96 percent yield by reducing IV or V with  $\text{LiAlH}_4$ , respectively. Infrared spectrum of VI showed a  $\nu(\text{C-O})$  at  $1053\text{ cm}^{-1}$  VII, m. 94-6°, was obtained in 49 percent yield by treating 2.7 g. IV with 4.5 g.  $\text{PCl}_5$  in  $\text{C}_6\text{H}_6$  under N atmosphere at 30-50°. VIII, m. 103-7°, was obtained in 68 percent yield by treating the mixture in IV preparation with activated  $\text{NaN}_3$  at room temperature IX, m. 75.5-7°, was obtained in 86 percent yield by heating VIII in PhMe at 80° for 4.5 hrs. IX showed a decomposing tendency corresponding to a decrease of intensity of  $\nu(\text{N:C:O})$  at  $2275\text{ cm}^{-1}$ . VI was treated with various diisocyanates in anisole at 155° for 3 hrs., and nonsoluble, yellow polymer, decomposing 180-245°, was obtained in 30-60 percent yield. The reaction of VI with tetramethylene diisocyanate (IX) in Ph Me at 110° for 1.5 hrs. gave a 75 percent polymer dissolving in  $\text{HCO}_2\text{H}$ . III also gave polymers soluble in  $\text{HCO}_2\text{H}$  by the reaction with IX in PhMe and anisole. The polymer prepared in PhMe in 11 percent yield decomposed at 170-80°, and the one prepared in anisole in 21 percent yield decomposed at 25-35°. V did not give a polyamide-type polymer by the reaction with various diamines. VII gave polymers decomposing 185-215° and 170-210° in 55 and 54 percent yield at 25° by an interfacial

polycondensation with hexamethylenediamine and tetramethylenediamine, respectively. The latter polymer was soluble in  $\text{HCONMe}_2$ . VIII was also made to react with various diamines and dioles in PhMe at  $110^\circ$  and gave 10-50 percent polymers which were soluble in  $\text{HCO}_2\text{H}$  and  $\text{HCONMe}_2$ . The N contents of all the polymers obtained above were approximately equal to that of a 1:1 addition or condensation product. The reduction-oxidation properties of these polymers were qualitatively examined by using  $\text{Ce}(\text{NO}_3)_4$ , quinone, and  $\text{HNO}_3$  as oxidizing agents and  $\text{TiCl}_3$  and ascorbic acid as reducing agents. The polyurethan-type polymer showed good reduction-oxidation properties, but the polyurea and the polyamide-type polymer were hardly oxidized.

484. Royal Aircraft Establishment, Farnborough, England,  
FERROCENE POLYMERS, PART I. A LITERATURE REVIEW  
by W. A. Lee, AD-269 708 (Unclassified Report).

The preparation and properties of addition, condensation, and recombination polymers of ferrocene are reviewed. There is a general lack of information about most of these systems. Uses have been claimed for some polymers as lubricants, adhesives, rubbers and plastics. The magnetic properties of some of these polymers are discussed. Forty-nine references are included.

485. Royal Aircraft Establishment, Farnborough, England,  
FERROCENE POLYMERS PART II. THE POTENTIALITIES  
OF 1,1'-DIMETALOFERROCENES FOR THE SYNTHESIS OF  
HIGH-TEMPERATURE RESISTANT POLYMERS by W. A. Lee,  
June 1962, Report No. RAE-CHEM-534, X63-10041 (Unclassified  
Report).

The potentialities of ferrocene compounds as precursors to high-temperature resistant polymers and the feasibility of using metaloferrocenes in their synthesis are discussed. Methods of preparation and reactions of metaloferrocenes are reviewed and suggestions made for further work on their synthesis. Preliminary reactions to establish the feasibility of polymerization reactions are recommended.

486. Royal Aircraft Establishment, Farnborough, England,  
FERROCENE POLYMERS. PART III. SOME ASPECTS OF  
THE REACTION BETWEEN FERROCENE AND PHENYLSODIUM  
by W. A. Lee and J. S. Pippett, July 1962, Report No.  
RAE-TN-CHEM-1400, X63-10044 (Unclassified Report).

The reaction of ferrocene with amylsodium and phenylsodium is discussed. Some effects of the method of preparation and purity of the phenylsodium, and of time and temperature variations on the metalation of ferrocene are reported. A reliable procedure for the synthesis of pure 1,1'-disodioferrocene free from monosodiocompounds was not found; some decomposition of the ferrocene moiety appears to occur during the reaction. The main product from a room-temperature reaction appears to be monosodioferrocene. The mixture of ferrocene and phenylsodium must be stored at room temperature before heating, to avoid very low yields of 1,1'-disodioferrocene and high yields of by-products. Recommendations for further work are outlined.

487. Royal Aircraft Establishment, Farnborough, England,  
FERROCENT POLYMERS. PART IV. ANHYDRIDES OF  
FERROCENE 1,1'-DICARBOXYLIC ACID by W. A. Lee,  
January 1963, Report No. RAE-TN-CPM-5, X63-13082  
(Unclassified Report).

As part of a search for high-temperature resistant polymers, ferrocene 1,1'-dicarboxylic acid anhydrides have been prepared from ferrocene 1,1'-dicarboxylic acid using acetic anhydride, and from ferrocene 1,1'-dicarboxylic acid chloride by hydrolysis. The mixed aromatic-aliphatic anhydride from the first reaction was unstable at room temperature, whereas the aromatic homoanhydride was stable at room temperature but lost 15 percent by weight at 250°F and 39 percent at 800°F.

488. Royal Aircraft Establishment, Farnborough, England,  
FRIEDEL-CRAFTS REACTIONS FOR THE SYNTHESIS OF  
HEAT RESISTANT AROMATIC POLYMERS by L. N. Phillips,  
April 1963, Report No. RAE CPM3, AD-417 958 (Unclassified Report).

Aromatic dichloromethyl derivatives can undergo condensation with linear aromatic polymers to bring about a cross-linking reaction, under mild conditions of temperature and catalyst concentration. Attack by the chloromethyl group on

ring hydrogen atoms is a principle capable of wide application to building polymer chains as well as cross-linking them.

The formation of soluble, fusible, intermediate polymers suitable for production of fibre-reinforced plastics was an important objective. Examples are given of the synthesis of polymers from aromatic hydrocarbons, borazoles, heterocyclic compounds and metallic derivatives. Typical resins from the more accessible molecules have been under evaluation as asbestos-reinforced laminates. The results of heat-ageing tests demonstrate that long-term stability in the temperature range 200-250°C, and a useful life of several hours at 400°C, are possible.

489. Royal Aircraft Establishment, Farnborough, England,  
NOTES ON THE INTERNATIONAL SYMPOSIUM ON MACROMOLECULAR CHEMISTRY, PRAGUE, 30 AUGUST 1965 - 4 SEPTEMBER 1965 by W. W. Wright, October 1965, Report No. TR-65233, AD-477 252 (Unclassified Report).

The symposium was organized under the auspices of the international union of pure and applied chemistry and was devoted to papers on fundamental research in all branches of the field of macromolecular chemistry. Features of the conference of particular interest to the work of chemistry, Physics and Metallurgy Department, Royal Aircraft Establishment, are briefly reviewed.

490. Sonogashira, K. and Hagihara, N.,  
SYNTHESIS OF THE FERROCENE DERIVATIVES HAVING CONJUGATED DOUBLE BOND SYSTEMS, Kogyo Kagaku Zasshi, Vol. 66, No. 8, 1963, pp. 1090-1094 (In Japanese) (Fc = ferrocenyl, Q = ferrocenediyl throughout this abstract).

Various ferrocene derivatives have been prepared for spectral study and oxidation potential measurements (Drefahl, et al., CA 58, 13989g). Condensation of 2.6 g. FcCHO (I) and 2.6 g p-xylylenebis(triphenylphosphonium) dichloride (II) in 15 ml. absolute EtOH in the presence of 25 ml. 0.4 N LiOEt-EtOH 5 hrs. at room temperature gave orange-red 200 mg. trans, trans-p-C<sub>6</sub>H<sub>4</sub>(CH:CHF<sub>c</sub>)<sub>2</sub>, m. 220° (decomposition) (C<sub>6</sub>H<sub>6</sub>), 130 mg. orange-yellow cis, cis-p-C<sub>6</sub>H<sub>4</sub>(CH:CHF<sub>c</sub>)<sub>2</sub>, m. 178-9°, and 200 mg. orange cis, trans-p-C<sub>6</sub>H<sub>4</sub>(CH:CHF<sub>c</sub>)<sub>2</sub>, m. 190° (decomposition). Similar reaction of 1.4 g. 1,1'-diformylferrocene (III) with 2.4 g. II gave 0.9 g. purple (-QCH:CHC<sub>6</sub>H<sub>4</sub>CH:CH-p-)<sub>7</sub>, m. 83-97°, molecular weight 2400

(cryoscopic,  $C_6H_6$ ). Reaction of 2 g. I with 3.9 g.  $[PhCH_2PPh_2Cl]$  (IV) gave 1.1 g. orange-red trans-FcCH:CHPh, m.  $123-5^\circ$ , and an orange-colored oil (presumably the cis isomer). III (0.7 g.) and 3 g. IV also gave 0.2 g. red-brown trans, trans-PhCH:CHQCH:CHPh, m.  $168-70^\circ$ . Refluxing 2.5 g. I with 3.7 g. 1,4-butylenbis(triphenylphosphonium) dibromide in 20 ml. tetrahydrofuran (THF) in the presence of 10 ml. N PhLi 7 hrs. gave 10 percent trans, trans-FcCH:CHCH<sub>2</sub>CH<sub>2</sub>CH:CHFc, m.  $200^\circ$  (decomposition). Arbuzov reaction of  $(EtO)_3P$  with  $ClCH_2CH:CHCH_2Cl$  in the presence of PhNMe<sub>2</sub> under N at  $130^\circ$  gave 53 percent  $[(EtO)_2P(O)CH_2CH:]_2$  (V),  $b_{15} 226^\circ$ . Condensation of 4 g. I and 3 g. V in 70 ml PhMe at  $120^\circ$  for 8 hrs in the presence of tert-BuOK, prepared from 1 g. K, gave 25 percent tan-red all-trans-(FcCH:CHCH:)<sub>2</sub> (VI), m.  $235^\circ$  (decomposition). Similarly, 2.4 g. FcCOMe and 1.7 g. V gave 0.3 g. red all-trans-(FcCMe:CHCH:)<sub>2</sub> (VII), m.  $235^\circ$  (decomposition), whereas 2.9 g. FcCOPh and 1.7 g V gave 0.9 g. tan-red all-trans-(FcCPh:CHCH:)<sub>2</sub> (VIII), m.  $205-20^\circ$  (decomposition). Attempted preparation of VI, VII, and VIII through Wittig reaction failed. Orange-red trans,trans-(FcCH:CH)<sub>2</sub>, m.  $230^\circ$  (decomposition), was prepared by the reduction of 1,4-diferrocenyl-2-butyne-1,4-diol with  $LiAlH_4$  in  $Et_2O$ . Condensation of 1.1 g. I with 0.26 g.  $(NCCH_2CH:)_2$  in refluxing absolute EtOH in the presence of EtONa for 2 hrs. gave 65 percent red-violet all-trans-(FcCH:C(CN)CH:)<sub>2</sub>, m.  $245^\circ$  (decomposition). Use of 1.5 g. III instead of I in the above gave a red-violet insoluble solid, possibly  $[-QCH:C(CN)CH:CHC(CN):CH-]_n$ , m.  $230^\circ$  (decomposition), in 60 percent yield. Knoevenagel reaction of 0.3 g. I and 0.1 g.  $CH_2(CN)_2$  in a solution of piperidine in absolute EtOH gave 77 percent deep violet FcCH:C(CN)<sub>2</sub>, m.  $100-1^\circ$  (petr. ether). Similarly, FcCOMe refluxed 3 hrs. with  $CH_2(CN)_2$  in absolute EtOH in the presence of  $NH_4OAc$  gave 50 percent red-violet FcCMe:C(CN)<sub>2</sub>, m.  $117-18^\circ$  (petr. ether). Reaction of 2 g. I with 0.43 g. p- $C_6H_4(NH_2)_2$  (IX) in refluxing absolute EtOH for 2 hrs. gave 80 percent brown p- $C_6H_4(N:CHFc)_2$ , m.  $250^\circ$  (decomposition), while 0.5 g. III with 0.32 g. IX yielded 60 percent red-brown  $(-QCH:NC_6H_4N:CH-p-)_n$ , m.  $250^\circ$  (decomposition). Similarly were prepared using benzidine, red-brown FcCH:NC<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>4</sub>N:CHFc, m.  $245^\circ$  (decomposition), and red-brown  $(-QCH:NC_6H_4C_6H_4N:CH-)_n$ , m.  $260^\circ$  (decomposition), both in 90 percent yields. Ultraviolet spectra of these compounds were given and discussed.



491. Valot, H. ,

POLYCONDENSATION OF FERROCENE AND FORMALDEHYDE,  
Comptes Rendus, Vol. 258, No. 24, 1964, pp. 5870-5872  
(cf. Panson and Watts, CA 57, 16650f).

Repetition of the reaction of ferrocene and paraformaldehyde, as studied by P. and W., led to the discovery of two polymers that are also formed. One is soluble, the other insoluble in  $C_6H_6$ . The soluble product has an infrared and elementary analysis suggestive of  $(-ZFeZCH_2-)_n$ , where Z is the ferrocenylene radical. The molecular weight, determined by b. p. changes, is 4800. The insoluble product appears to contain O and is probably cross-linked through hydroxymethyl groups.

492. Valot, H. ,

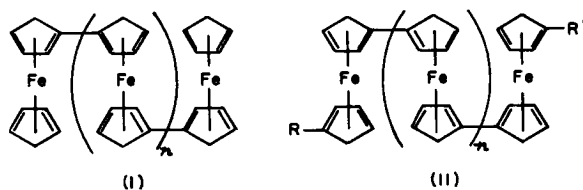
SYNTHESIS OF THE POLYESTERS OF FERROCENE-1,  
1'-DICARBOXYLIC ACID BY PYRIDINATED POLYACYLATION  
OF VARIOUS DIOLS, Comptes Rendus Series, Vol. 262, No. 5,  
1966, pp. 403-405 (In French) (cf. Knobloch and Raucher,  
CA 56, 2561c).

A solution of 0.005 mole 1,10-decanediol (I), 1,6-hexanediol (II),  $p-C_6H_4(CH_2OH)_2$  (III), or 1,1'-bis(hydroxymethyl)ferrocene (IV) in 3-5 ml. anhydrous pyridine was added in 20-30 min. to a solution of 1.55 g. (0.005 mole) of ferrocene-1,1'-dicarbonyl chloride in 20 ml. dry PhMe. The reaction mixture was stirred for 20-4 hrs. in an inert atmosphere in the absence of light at  $70-5^\circ$ . When the polycondensate was soluble (I and II), the reaction mixture was filtered and the filtrate was slowly poured into EtOH containing a small amount of HCl. The precipitate was dissolved in  $C_6H_6$  and the solution was again poured into the alcoholic HCl. The precipitate was washed and dried. When the polycondensate was insoluble (III and IV), the reaction mixture was filtered and the precipitate was washed on the filter with PhMe and then with  $H_2O$ . It was finally washed with EtOH, with reflux. The polyesters prepared,  $[OCC_5H_4FeC_5H_4CO_2RO]_n$ , are shown in the table. For polycondensates of I and II, the most satisfactory hypothesis was the existence of primary alcoholic groups at the ends of the chains; for III and IV, carboxylic groups.

Diol	R	Yield, %	Av. n	Calcd.	Meas. Mol. Wt.	Appearance
I	$(\text{CH}_2)_{10}$	19	11	4709	----	brown, pasty solid
II	$(\text{CH}_2)_6$	31	4	1543	6280	yellow powder, m. 68-72°
III	$\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2$	83	4	1779	----	yellow powder, m. 200° (decom- position)
IV	$\text{Fe}(\text{C}_5\text{H}_4\text{CH}_2-)_2$	56	4	2210	----	yellowish-brown powder, becoming brown at 170°, m. 180° (decomposi- tion).

493. Watanable, H., Motoyama, I., and Hata, K.,  
DIRECT FORMATION OF BIFERROCENYL AND POLYFERRO-  
CENYLS FROM FERROCENYLLITHIUM, Chemical Society of  
Japan Bulletin, Vol. 39, No. 3, 1966, pp. 790-801 (Fc = ferro-  
ceny throughout this abstract).

FcLi treated with  $\text{CoCl}_2$  in the presence or absence of  
BuBr yielded various I ( $n = 0-4$ ) and II ( $n = 0-2$ , R and  
R' = Bu and (or) H). The compounds were formed by coupling  
of the Fc radical, the ferrocenylene radical, and the Bu radical



which were generated by the homolytic fission of some reactive  
intermediate and Bu halide. The presence of BuCl greatly  
affected the type and yield of the products. No cyclic polyferro-  
cenylenes were obtained. The 9-10 rule covering the infrared  
spectra of the derivatives of ferrocene (III) was found not to  
apply to disubstituted  $\text{Fc}_2$ . The x-ray diffraction patterns and  
the infrared spectra demonstrated that I ( $n = 1$ ) (IV) crystallizes  
in polymorphic forms depending on the method and the solvent  
of crystallation. The polymorphism may be attributed to the  
rotational isomerism around the central III nucleus. FcLi  
from 55.8 g. III and 0.6 mole BuLi in dry  $\text{Et}_2\text{O}$  treated under  
N with 9.1 g.  $\text{CoCl}_2$  and then 14.4 g. BuBr followed by an  
additional 26.70 g. BuBr, stirred 44 hrs at room temperature,  
and refluxed 1 hr., the mixture poured into iced  $\text{H}_2\text{O}$ , and the  
precipitate filtered off and extended about 100 hrs. in a Soxhlet  
apparatus with  $\text{Et}_2\text{O}$  and then triturated with 1.5 l. boiling

$C_6H_6$  in several portions left 5.6 g. gray, inorganic residue; the residue from the combined  $C_6H_6$  and  $Et_2O$  extracts extracted fractionally with benzene and the various fractions chromatographed gave 0.67 g. I ( $n = 4$ ), m.  $252-6^\circ$ ; 2.426 g. I ( $n = 2$ ), m.  $280^\circ$  ( $C_6H_6$ ); 0.46 g. VI, m.  $228-31^\circ$  ( $C_6H_6$  - petroleum ether); about 220 mg. VII; 2.12 g. IV, m.  $214-20^\circ$ ; 0.16 g. orange-red II ( $R = Bu$ ,  $R' = H$ ,  $n = 2$ ), m.  $177-9^\circ$ ; 0.337 g. dark-red glass; and 55 mg. light-brown powdery I ( $n = 3$ ), m.  $240-5^\circ$  ( $C_6H_6$ ). The original filtrate separated the aqueous phase extracted with  $Et_2O$ , the  $Et_2O$  phase and extract evaporated, and the residue sublimed gave 35.6 g. unreacted III and left 15.5 g. orange-red residue which chromatographed on  $Al_2O_3$  yielded 0.22 g. orange II ( $n = 0$ ,  $R = R' = Bu$ ), m.  $52.3^\circ$ ; 2.17 g. red-orange II ( $R = Bu$ ,  $R' = H$ ,  $n = 0$ ) (V), m.  $68-70^\circ$ ; 5.78 g. I ( $n = 0$ ) (VI), m.  $225-34^\circ$  (decomposition); 0.34 g. II ( $R = Bu$ ,  $R' = H$ ,  $n = 1$ ) (VII), m.  $113-15^\circ$ ; 1.54 g. orange IV, m.  $226.5-7.2^\circ$  ( $C_6H_6$  - petroleum ether); and 1.0 g. dark-red glass.  $FcLi$  from 55.8 g. III and 0.6 mole  $BuLi$  treated with 9.1 g.  $CoCl_2$ , cooled to room temperature during 3 hrs., and stirred 70 hrs. under  $N$  at room temperature, and the crude product extracted 8 hrs. with  $Et_2O$  in a Soxhlet apparatus left 7.77 g. gray-black inorganic solid; the residue from the extract sublimed at  $100-20^\circ/0.5$  mm. yielded 53.4 g. unreacted III and left 2.33 g. dark red-brown solid which chromatographed on  $Al_2O_3$  yielded 0.38 g. V, m.  $67-9^\circ$ ; 1.06 g. VI, m.  $228.5-33^\circ$ ; 59 mg. orange butyl-polyferrocenyl; 0.14 g. IV, m.  $215-18^\circ$ ; and 0.2 g. dark red-brown glass. The infrared spectra of the various I and II are recorded.

494. Yarsley Research Laboratory Limited, Great Britain,  
FEASIBILITY STUDY ON THE PREPARATION OF PARAMAGNETIC POLYMERS BASED ON FERROCENE-TYPE COMPOUNDS by W. Flavell, AD-268 357 (Unclassified Report).

Magnetic Properties, Stability. (Chemical reactions, condensation reactions, polymerization, substitution reactions.) A study of the preparation of magnetic polymers based on ferrocene-type compounds was conducted. From a consideration of molecular dimensions it was concluded that ferromagnetism is not possible in polymers based on ferrocene or its analogues. Polymers based on the paramagnetic analogues were studied and synthesis of these polymers was investigated. The properties of the paramagnetic ferrocene analogues were surveyed and it was concluded that the Ni compound was the best source in the preparation of paramagnetic polymers.

Possible routes to such polymers were experimentally studied: 1) The reaction of a dicyclopentadienyl alkane with a Ni halide 2) The preparation of vinyl nickelocene and its polymerization 3) The arylation of nickelocene by means of diazonium salts 4) The preparation of ionic polymers of ferrocene.

## A. Chromatography

495. Bozak, R. E.,  
ACETYLATION OF FERROCENE; CHROMATOGRAPHY  
EXPERIMENT FOR ELEMENTARY ORGANIC LABORATORY,  
Journal of Chemical Education, Vol. 43, No. 2, 1966, p. 73.

Ferrocene (I), 3 g., 10 ml.  $\text{Ac}_2\text{O}$ , and 2 ml. 85 percent  $\text{H}_3\text{PO}_4$  heated 10 min. on the steam bath, the whole poured on ice, the pH adjusted to seven with  $\text{NaHCO}_3$ , and cooled gave a brown solid (II). The II (0.3 g.) in 1.5-2.0 ml.  $\text{C}_6\text{H}_6$  (III) placed on an  $\text{Al}_2\text{O}_3$  column, and the column eluted with petroleum ether (IV) gave unreacted I; elution with III or IV- $\text{Et}_2\text{O}$  gave acetylferrocene.

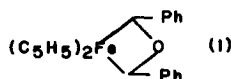
496. Nesmeyanov, A. N. and Kritskaya, I. I.,  
FORMATION OF ETHERS OF FERROCENEMETHANOLS AND  
THEIR HYDROLYSIS UNDER THE CONDITIONS OF ADSORP-  
TION CHROMATOGRAPHY, Izvestiya Akademii Nauk SSSR,  
Seriya Khimicheskaya, No. 12, December 1964, pp. 2160-2165.

Refer to item No. 349 for abstract.

497. Nesmeyanov, A. N., Kritskaya, I. I., and Antipina, T. V.,  
APPLICATION OF ADSORPTION CHROMATOGRAPHY TO  
FERROCENE DERIVATIVES, Izvestiya Akademii Nauk, SSSR,  
Otdeleniye Khimicheskikh Nauk, 1962, pp. 1777-1783.

Ferrocenes with  $\text{ArCH}_2$  or  $\text{RCHOH}$  substituents are readily oxidized by air on  $\text{Al}_2\text{O}_3$  and form the corresponding ferrocenyl aryl (alkyl) ketones. On  $\text{SiO}_2$  the oxidation affects most readily the ferrocene compounds which have electron donor groups and converts them into ferricinium cations. Ferrocenylcarbinols undergo disproportionation on  $\text{SiO}_2$ , as well as loss of  $\text{H}_2\text{O}$ , to form ethers. Polyarylmethylcarbinols also form ethers under such conditions. The following ferrocene derivatives are reported: benzylferrocene, m. 75-6°; benzoylferrocene, m. 105-7°; ferrocenylphenylcarbinol, m. 80-1°; bis ( $\alpha$ -hydroxybenzyl) ferrocene, m. 134-6°; methylferrocenylcarbinol, m. 75.-6°; sym-diphenyldifferocenyethane, m. 229° and m. 271° (diastereomers). Bis ( $\alpha$ -hydroxybenzyl)-ferrocene on  $\text{SiO}_2$  under such conditions gave I, m. 195-7°, and II which on

reduction with  $\text{SmCl}_2$  gave I. Phenylferrocenylcarbinol on  $\text{SiO}_2$  gave benzylferrocene, benzoylferrocene, 27 percent substance, m.  $130-1^\circ$ , and 30 percent benzylferrocenium and hydroxybenzylferrocenium ions. Phenylferrocenecarbinol in MeOH on  $\text{SiO}_2$  gave 98 percent  $\alpha$ -methoxybenzylferrocene, m.  $113-14^\circ$ . Methylferrocenylcarbinol on  $\text{SiO}_2$  gave 31 percent ethylferrocene, trace of acetylferrocene, a substance, m.  $145^\circ$ , and some ethylferrocenium ions. In the presence of MeOH the product was 58 percent  $\alpha$ -methoxyethylferrocene, m.  $24-6^\circ$ . Diphenylcarbinol on  $\text{SiO}_2$  gave dibenzhydriol ether, while benzyl alcohol was unchanged.



498. Organisch-Chemisches Institute, Wien University, Austria, CONFERENCE ON HIGH TEMPERATURE POLYMER AND FLUID RESEARCH, RESEARCH ON ORGANIC CHEMISTRY OF FERROCENE by K. Schlogel, August 1962, X63-15745, Directorate of Materials and Processes, Wright-Patterson Air Force Base, Ohio, pp. 571-595 (X63-15709 22-07) (Unclassified Report).

Surface chromatography on silica gel (Kieselgel-G) using benzene-ethanol mixtures or hexane as solvents has proved to be a very useful analytical method for rapid separation and identification of ferrocene derivatives.

499. Redstone Scientific Information Center, Redstone Arsenal, Alabama, THIN-LAYER CHROMATOGRAPHY OF FERROCENE DERIVATIVES by K. Schlogel, H. Pelousek, and A. Mohar, January 1966, RSIC-511, AD-478 285L (Unclassified Report).

Thin-layer chromatography proved to be very suitable for the fast separation and identification of ferrocene derivatives. Chromatographed on silica gel were a total of 49 ferrocenylketones, ferrocenylcarbinols and ferrocenylglycoles, ester, ether, and n-containing derivatives of the ferrocenes, and also alkylferrocenes and alkenylferrocenes. Excellent separations were obtained, especially in mixtures of benzol and benzol-ethanol. The  $R_F$ -values of these compounds were compiled graphically in five illustrations.

500. Tanikawa, K. and Arakawa, K.,  
ORGANOMETALLIC COMPOUNDS. IV. ANALYTICAL  
DETERMINATION OF FERROCENE DERIVATIVES BY GAS  
CHROMATOGRAPHY, Chem. Pharm. Bull. (Tokyo), Vol. 13,  
No. 8, 1965, pp. 926-931.

The following compounds were prepared: ferrocene (I), 1,1'-diacetylferrocene (II), di-Me 1,1'-ferrocenedicarboxylate (III), acetylferrocene (IV), ferrocenemethanol (V), 1,1'-ferrocenedimethanol (VI), ferrocenemercury chloride (VII), iodoferrocene (VIII), and phenylferrocene (IX). Analyses and determinations of purity of the ferrocene derivatives were made by ir spectroscopy, thin-layer chromatography, and N.M.R. spectroscopy. The following columns were employed: (A) 1 percent SE-30 on Chromosorb W; (B) 0.5 percent SE-30 on glass microbeads; (C) one percent SE-52 on glass microbeads; (D) 2.5 percent SE-52 on glass microbeads; (E) one percent polyethylene glycol succinate (PEGS) on Chromosorb W; (F) 2.5 percent PEGS on Chromosorb W; (G) 2.5 percent polyethylene glycol 6000 on Chromosorb W; (H) 2.5 percent Apiezon-L on Chromosorb W. Retention times (min.) of I-IX on columns A-H were tabulated; the column temperature of column H was 200°, and 190° in columns A, B, F, G, 170° in columns C and E, and 180° in column D; He was introduced as carrier gas at 30-100 ml./min.; samples were injected in CHCl<sub>3</sub>. A mixture of I and IX was separated, by any of columns A-H, the results obtained using columns A, F, and H being compared. In the process of acetylation of I, II, and IV are formed and unchanged I is present. This mixture was separated by any of columns A-H, results being shown for columns A and H which give very symmetrical peaks. In the synthesis of VI from I [Schlogel, et al., *Monatsh. Chem.* 92, 533 (1961)], I and the intermediates II and III are present in the product. This mixture was separated only by column H. In the synthesis of biferrocenyl, I and the intermediates VII and VIII were present in the product. This mixture was satisfactorily separated by any of columns A-H.

501. Aeronautical Systems Division, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio,  
X-RAY POWDER DIFFRACTION DATA FOR SOME FERROCENE DERIVATIVE by W. L. Baun and M. Goldschmidt, , November 1962, Report No. TDR62 874, AD-292 011 (Unclassified Report).

Application of X-ray diffraction to identification of polycrystalline ferrocene derivatives is discussed. These compounds are well suited to X-ray diffraction analysis because of their crystalline nature and the individualistic patterns obtained even in closely related substitutions. Data are shown for various mono and disubstituted compounds. Emphasis is placed on effects noted in long chain substitutions and spacings are given for 12 of this type of compound. Powder diffraction data and other physical properties are shown for 20 ferrocene derivatives which were synthesized for research on ultraviolet absorbers for space vehicles.

502. Aeronautical Systems Division, Materials Laboratory, Wright-Patterson Air Force Base, Ohio,  
X-RAY CRYSTALLOGRAPHIC AND POWDER DATA FOR SOME FERROCENIC DERIVATIVES by D. W. Fischer, February 1964, Report No. TDR64 23, AD-433 231 (Unclassified Report).

Results are shown for X-ray crystallographic and X-ray powder diffraction analysis of ferrocene and 14 ferrocene derivatives. Data include lattice parameters, space group, molecules per cell, density, melting point, color, formula, and indexed power pattern of each compound.

503. California University, Department of Chemistry, Los Angeles, California,  
THE CRYSTAL AND MOLECULAR STRUCTURE OF 1,1'-TETRAMETHYLETHYLENEFERROCENE by M. B. Laing and K. N. Trueblood, August 1964, Report No. AFOSR 65-2387, AD-627 955, Contract No. AF49(638)-719 AF-9762 976201 (Unclassified Report).

1,1'-Tetramethylethyleneferrocene forms monoclinic plates of space group  $P2_1/C$ , and four molecules in the unit cell with  $A = 7.756$ ,  $B = 10.97$ ,  $C = 15.41$ , and  $\text{Beta} = 92.63$  degrees. The structure was solved from three-dimensional



Patterson and Fourier syntheses, and was refined by Block-Diagonal least squares.

The two 5-membered rings are tilted 23 degrees with respect to one another, but because of the bridge linking them are staggered only by about nine degrees, in contrast to ferrocene. The strain in the molecule is apparent also in the fact that the dihedral angles in the bridge are only about 26 degrees, and that the exocyclic bonds are bent about 11 degrees from the ring planes. The bond distances in the bridge are slightly greater than normal. The bond distances in the ring and to the iron atom appear normal.

504. California University, Los Angeles, California,  
STUDY OF THE MOLECULAR AND CRYSTAL STRUCTURE  
OF ORGANIC COMPOUNDS OF UNUSUAL GEOMETRY OR  
ELECTRONIC STRUCTURE, FINAL REPORT, JANUARY-  
DECEMBER 1963 by K. N. Trueblood, April 1964,  
Report No. AFOSR 64 1107, AD-601 478, Contract No.  
AF AFOSR240 63 (Unclassified Report).

The report includes further development of applications of high-speed computers in crystallographic structure work. A description is given of a precise study of the structure of tetracyanoquinodimethane, heteroaromatic dibenzo-1, 3A, 4, 6A-tetraazapentalene, an aminotroponeimine derivative with aromatic properties, and a ferrocene derivative in which the two cyclopentadienyl rings are joined by a two-carbon bridge. Preliminary reports are given of reinvestigations of the structures of tetracyanoethylene and di-p-xylylene. A description of the structure of the hydrated calcium salt of the unusual acid hexacyanoisobutylene. The anion of this acid is highly stabilized by resonance, and preliminary considerations might suggest that it should be planar; in fact, however, we find it to be propeller-shaped, with the arms tilted about 24 degrees, this tilt does not reduce the pi-overlap very much and does relieve intramolecular steric strain considerably.

505. California University, Los Angeles, California,  
X-RAY STUDIES OF UNUSUAL ORGANIC COMPOUNDS, FINAL  
REPORT, 1 SEPTEMBER 1959-31 DECEMBER 1962 by D. A.  
Bekoe, M. E. Burke, C. L. Coulter, and P. K. Gantzel,  
March 1963, Report No. 5135 (Unclassified Report).

Contents: Unpublished work-the crystal structure of  
5-keto-1, 5-dihydrobenz (CD) indole; the crystal structure of

the hexahydrated calcium salt of hexacyanoisobutene; the crystal structure of the cubic form of tetracyanoethylene; the crystal structure of 1, 1'-(tetramethylethylene) ferrocene; miscellaneous structural studies; and crystallographic computing.

Reports and publications-crystallographic calculations on SWAC and on the IBM 709; comparison of various least squares refinement techniques; crystal structure of the diolefin of (2. 2) paracyclophane; crystal structure of trimethyloxosulfonium perchlorate; and crystal structure of (3. 3) paracyclophane.

506. Dabard, R. and Weigel, D.,  
STRUCTURAL INVESTIGATION OF CERTAIN SUBSTITUTED  
FERROCENES, Societe Chimique de France. Bulletin, Vol. 1,  
1966, pp. 390-396 (In French).

The structures of a number of crystallized ferrocenes were studied by X-ray diffraction in a CGR  $\theta$  60 diffractometer with Fe radiation. The values of  $d(A)$  and  $I/I_{max}$  for the series  $\alpha_1$ ,  $\alpha_2$ , and  $\beta$  are tabulated for  $\beta$ -ferrocenyl- $\alpha$ -methylpropionic acid (I),  $\beta$ -ferrocenyl- $\beta$ -methylpropionic acid,  $\beta$ -ferrocenyl- $\beta$ -phenylpropionic acid (I),  $\beta$ -ferrocenyl- $\alpha$ -phenylpropionic acid,  $\beta$ -(3,1'-diethyl-1-ferrocenoyl)propionic acid,  $\beta$ -(2,1-diethyl-1-ferrocenoyl)propionic acid, 2,3-ferroceno-6-phenyl-2-cyclohexene-1-one, p-tolyl ferrocenyl ketone, 2-thienylferrocenyl ketone, 2-pyrrolyl ferrocenyl ketone, 1-acetyl-3-methylferrocene, 1'-ethyl-2,3-ferroceno-2-cyclohexene-1-one, 1-(phenylacetyl)ferrocene-1'-carboxylic acid,  $\beta$ -(1'-acetyl-1-ferrocenoyl)propionic acid, and 1,1'-bis(2-hydroxy-1-phenylethyl)ferrocene. The chemical and structural identity of two specimens of I of different m.p.s. was established. Differences in intensities in the different series for some samples are thought to be due to the flat shape of the grains of the powder causing preferred orientation.

507. Fischer, D. W.,  
CRYSTALLOGRAPHIC DATA FOR SOME FERROCENE  
DERIVATIVES, Acta Crystallographica, Vol. 17, No. 5, 1964,  
p. 619.

X-ray powder diffraction d., and m.p. data, of ferrocene and 14 derivatives gave the following crystallographic data ( $a, b, c, (A), \beta$ , space group, Z, d. (experimental), d. (calculated), and m.p., respectively). Ferrocene: 10.56, 7.597, 5.952,  $121^\circ$ ,  $P2_1/a$ , 2, -, 1.516, -. Et ferrocenoate: 5.89, 11.13, 17.91, -,  $P2_12_12_1$ , 4, -, 1.454,  $63.0-64.0^\circ$ . Ph ferrocenoate:

the orthorhombic system and the Pbc<sub>a</sub> space group; Z = 8. IV (m.p. 143°) was unstable in most organic solutions and could only be crystallized from petroleum ether. It crystallized in the monoclinic system and the P2<sub>1</sub>/c space group, and Z = 4. V (m.p. 83-83.5°) crystallized from petroleum ether and was decomposed by x-radiation. It crystallized in the orthorhombic system and Pbc<sub>a</sub> space group, with Z = 8. VI (m.p. 116-117°) was crystallized from pyridine and was stable under ordinary conditions and to x-rays; it crystallized in the monoclinic system and the P2<sub>1</sub>/n space group with Z = 8. VII (m.p. 196°) crystallized in the orthorhombic system and Pccn space group; and Z = 8. VIII (m.p. 135-136°) crystallized from xylene was stable and belonged to the monoclinic system and the P2<sub>1</sub>/c space group; Z = 2. Two modifications differing in unit cell dimensions but having the same d. and belonging to the P2<sub>1</sub>/c space group were distinguished: the previously studied (CA 62, 15528h) α-form, bis[1-(2'-chloro)-ferrocenyl], and the β-form described here, bis[1-(1'-chloro)-ferrocenyl], which did not crystallize out together. IX (m.p. 184-4.5) also crystallized from xylene in 2 forms: the α-modification (~70 percent by volume of the crystal mass) and the β-modification (~30 percent of the crystal mass). Both forms crystallized in the monoclinic system, the α-form in the P2<sub>1</sub>/c space group and the β-form in the P2<sub>1</sub>/n space group. The α- and β-forms differed in unit-cell volume by three percent and crystallized out together from solution. Unit-cell dimensions, molecule weights, and d. data are given for each compound.

510. Kaulski, Z. L. and Struchkov, Y. T.,  
INTERMOLECULAR DISTANCES AND PACKING OF MOLECULES IN CRYSTAL OF BIS-[1'-(1-ETHYLFERROCENYL)],  
Zhurnal Strukturnoi Khimii, Vol. 7, 1966, pp. 283-286.

Not abstracted.

511. Kaluski, Z. L., Struchkov, Y. T., and Avoyan, R. L.,  
X-RAY STUDY OF THE DIFERROCENYL STRUCTURE,  
Journal of Structural Chemistry (USSR), Vol. 5, 1964, p. 683.

Refer to item No. 68 for abstract.

512. Koplev, Y. F. and Vainshtein, E. E.,  
DETERMINATION OF THE EFFECTIVE CHARGE ON THE  
IRON ATOMS IN SOME POLYFERROCENES FROM THE  
SPECTRA OF X-RAY ABSORPTION, Akademii Nauk SSSR,  
Sibirskoye Otdeleniye. Izvestiya, Ser. Khim. Nauk, Vol. 2,  
1964, pp. 3-9 (In Russian).

The effect of polymerization on the distribution of electron d. in polyferrocene (I), poly(butylferrocene) (II), poly(dibutylferrocene) (III), poly(amylyferrocene) (IV), and poly(diisopropylferrocene) (V) was investigated. A new method was derived for the determination of  $\eta/n$  ( $\eta$  = effective charge of the K-ionized atom in the molecule;  $n$  = effective principal quantum number of the level on which the K electron is transferred) without decomposition of the spectra in their components. For  $n$  = construction, the effective nuclear charge decreased in the series  $\text{Fe}(\text{C}_5\text{H}_5)_2 - \text{Fe}(\text{C}_5\text{H}_5)_2\text{Cl} - (\text{I-IV}) - \text{V}$ . When the effective at. charge decreased, the ratio of the long-wave absorption band intensity ( $\tau'$ ) to the first band of the H-like series intensity ( $\tau''$ ) increased. The  $\tau'/\tau''$  values were -0.58 in ferrocene, -0.68 in ferricinin, -0.70 in I-IV, and -0.89 in V.

513. MacDonald, A. C. and Trotter, J.  
THE CRYSTAL AND MOLECULAR STRUCTURE OF BIFERRO-  
CENYL, Acta Crystallographica, Vol. 17, 1964, p. 872.

Refer to item No. 69 for abstract.

514. Vainshtein, E. E. and Koplev, Y. F.,  
X-RAY SPECTROSCOPY STUDY OF CERTAIN POLYFERRO-  
CENES, Akademii Nauk, SSSR Doklady, Vol. 149, No. 6,  
1963, pp. 1360-1363.

X-ray spectra of polyferrocene (1), poly(butylferrocene) (2), poly(dibutylferrocene) (3), poly(amylyferrocene) (4), and poly(diisopropylferrocene) (5) were studied. The object of the study was to determine the polymerization effect on the character of charge distribution between metal and ligands of different polymeric molecules. With  $n$  (effective quantum no. of a final equation of transition of K electron) the magnitude of effective charge on the Fe atom decreased in the order one to five.

515. Army Electronics Command, Fort Monmouth, New Jersey, ELECTRONICALLY FUNCTIONAL ORGANIC MATERIALS, TECHNICAL REPORT by G. Platau, W. R. Wenger, and E. Beekman, September 1964, Report No. ECOM-2508, AD-609 831 (Unclassified Report).

The syntheses of 14 compounds based on ferrocene, nickelocene, and Cyclopentadiene are described. The infrared spectra for these compounds are shown. Conductivity and electron spin resonance absorption measurements performed on these and 12 other compounds obtained from external sources indicate poor electronic activity for most of these materials. The application of these compounds and organic compounds in general as active elements in electronic devices is discussed.

516. Kazakova, V. M. and Syrkin, Y. K., HYPERFINE STRUCTURE OF THE ELECTRON PARAMAGNETIC RESONANCE (E. P. R.) SPECTRA OF METAL KETYLs, Zhurnal Strukturnio Khimii, Vol. 3, 1962, pp. 536-540.

The E. P. R. spectra of metal ketyl radicals formed by a reaction of alkali metals with ketones were investigated. Aliphatic and aromatic ketones, quinones, and benzoylferrocene were used. Starting from the hyperfine structure analysis it was shown that the stability of aromatic radicals is increased by the delocalization of the unpaired electron. In the aliphatic radicals the uncoupled electron is localized on the C atom of the CO group, and the stability can be enhanced by the steric effect.

517. Levenberg, M. I.,

I. PRELIMINARY STUDIES OF THE CHAIN-TRANSFER CONSTANT OF METHYLFERROCENE. II. PROTONATION OF METALLOCENES. III. AN ANALYSIS OF THE N.M.R. SPECTRA OF SUBSTITUTED FERROCENES. IV. EXPERIMENTAL AND THEORETICAL STUDIES OF THE CHARGE DISTRIBUTION OF THE FERROCENYL CARBINYL CARBONIUM ION, Dissertation Abstract, Vol. 26, April 1966.

#### PART I

Styrene monomer containing various concentrations of methylferrocene was allowed to polymerize at 70°C. The average molecular weight of the resulting polystyrene was determined, and the chain transfer constant of methylferrocene then calculated. The constant was found to be  $0.7 \times 10^{-4}$ , indicating some contribution to the stability of the methyl free radical by the ferrocenyl group.

The reactivity of methylferrocene to free radical attack is discussed, and the copolymerization of methylferrocene with styrene is considered.

#### PART II

The N.M.R. spectra of ferrocene, ruthenocene, and osmocene in boron trifluoride monohydrate have been studied. Accurate measurements of relative peak areas and positions are reported. The species responsible for the N.M.R. spectra are discussed.

#### PART III

A detailed analysis of the N.M.R. spectra of a series of alkylacetylferrocenes in a variety of solvents has been carried out. This has allowed a determination of the coupling constants between the various protons in these substances. For protons attached to the same ring, the following values are generally observed:  $J_{23} \sim 2.5$  cps and  $J_{24} \sim 1.3$  cps. The magnetic anisotropy of the carbonyl group in 2-acetyl-1,1'-trimethylene ferrocene is also discussed.

#### PART IV

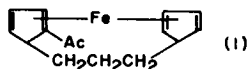
The existence of the stable ferrocenylcarbinyl carbonium ion has been demonstrated by freezing point depression measurements in concentrated sulfuric acid. The N.M.R. spectrum of the carbonium ion has been observed and the chemical shifts

of its protons relative to those of methylferrocene have been measured. The factors influencing the proton chemical shifts are discussed.

Techniques of molecular orbital calculations applicable to ferrocenyl systems are discussed and the results of a series of molecular orbital calculations on the ferrocenylcarbinyl carbonium ion are presented. The chemical shifts of the protons on the carbonium ion are predicted from the molecular orbital calculations, and the predictions are compared with the experimentally measured chemical shifts. The agreement is not good as could be desired.

518. Levenberg, M. I. and Richards, J. H.,  
AN ANALYSIS OF THE NUCLEAR MAGNETIC RESONANCE  
SPECTRA OF SUBSTITUTED FERROCENES, Journal of  
American Chemical Society, Vol. 86, No. 13, 1964, pp. 2634-  
2637.

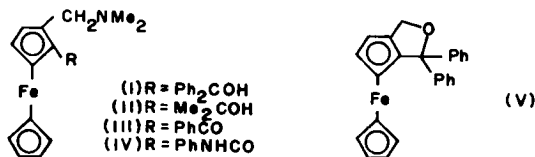
A detailed analysis of the nuclear magnetic resonance spectra of a series of alkylacetylferrocenes in a variety of solvents was carried out. This allowed a determination of the coupling constructions between the various protons in these



substances. For protons attached to the same ring, the following values were generally observed:  $J_{23}$  2.5 cycles/sec. and  $J_{24}$  1.3 cycles/sec. The magnetic anisotropy of the CO group in 2-acetyl-1, 1'-trimethyleneferrocene (I) was also discussed.

519. Smith, P., McLeskey, J. J., III, and Slocum, D. W.,  
MAGNETIC NONEQUIVALENCE OF METHYLENE-GROUP  
PROTONS IN 1,2-DISUBSTITUTED FERROCENES, Journal  
of Organic Chemistry, Vol. 30, No. 12, 1965, pp. 4356-4357.

The N. M. R. spectra of the 1,2-disubstituted ferrocene analogs (I-V) of five previously studied sym. 0-substituted



benzene derivatives were obtained. As expected, all five compounds displayed magnetically nonequivalent methylene-group protons.

520. Utyanskaya, E. Z.,  
PROTON MAGNETIC RESONANCE SPECTRUM FOR PENTA-ETHANODIFERROCENE, Zhurnal Fizicheskai Khimii, Vol. 35, 1961, pp. 2611-2612.

An analysis of the proton resonance spectrum of penta-ethanodiferrocene in concentrated  $C_6H_6$  solutions led to the conclusion that the intermolecule spin-spin interactions, i. e., the interaction of the magnetic moments of the protons within a single molecule make the major contribution to the relaxation time for the protons of the  $CH_2$  groups, in the ethane bridges. The observed ratio of  $\Delta\nu'/\Delta\nu'' \leq 1/5$ , where  $\Delta\nu''$  and  $\Delta\nu'$  are the widths of the spectrum lines belonging to protons of the  $CH_2$  groups and the protons of the ferrocene ring, respectively, does not contradict the structure proposed by Nesmeyanov and Kochetkova (CA 53, 21856g).

#### D. Infrared and Ultraviolet (Visible) Spectroscopy

521. Bailey, R. T. and Lippincott, E. R.,  
THE VIBRATIONAL SPECTRUM OF DIMETHYLFERROCENE, Spectrochimica Acta, Vol. 21, No. 3, 1965, pp. 389-398.

The ir ( $4000-250\text{ cm.}^{-1}$ ) and Raman (up to  $1650\text{ cm.}^{-1}$ ) spectra of dimethylferrocene are reported. The Raman spectrum was excited by a radio-frequency-powered Rb plasma arc. The spectra were consistent with a model involving little interaction between the methylcyclopentadienyl rings and having pseudo  $C_{2v}$  symmetry. A reasonable assignment of the fundamental vibrations, based on this model, was made by comparison with ferrocene and toluene and utilizing the inequality rule proposed by Steele and Whiffen (CA 54, 2008i). The assignment was also consistent with the modified product rule due to Pitzer and Scott (CA 37, 4297<sup>5</sup>).



522. Fritz, H. P.,  
INFRARED AND RAMAN SPECTRAL STUDIES OF  $\pi$  COM-  
PLEXES FORMED BETWEEN METALS AND  $C_NH_N$  RINGS,  
Advances in Organo-Metallic Chemistry, New York, New  
York, Academic Press, Vol. 1, 1964, pp. 239-316.

This review covers 158 references. The coverage is very broad covering other metals than iron and mono-ring metal compounds as well as various ring systems besides cyclopentadiene.

#### CONTENTS

- I. Introduction
- II. Theoretical Considerations in the Analysis of Vibrational Spectra
- III. Techniques of Infrared and Raman Spectroscopy
- IV. General Aspects of the Analysis of Spectra of  $\pi$  Complexes of Cyclic Systems,  $C_nH_n$
- V. Experimental Results for Three-Membered Rings
- VI. Experimental Results for Four-Membered Rings
- VII. Experimental Results for Five-Membered Rings
- VIII. Experimental Results for Six-Membered Rings
- IX. Experimental Results for Seven-Membered Rings
- X. Experimental Results for Eight-Membered Rings
- XI. Some Quantities Derived from Vibrational Spectra

523. Grandberg, K. I. and Gubin, S. P.,  
ABSORPTION SPECTRA OF HETEROANNULAR DISUBSTITUTED  
FERROCENES, Izvestiya Akademii Nauk SSSR, Seriya  
Khimicheskaya, 1966, pp. 551-554.

Not abstracted.

524. Grandberg, K. I., Gubin, S. P., and Perevalova, E. G.,  
EFFECTS OF SUBSTITUENTS ON THE ABSORPTION BAND  
SHIFTS IN THE SPECTRA OF MONOSUBSTITUTED FERRO-  
CENES, Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya,  
1966, pp. 549-551.

Not abstracted.

525. Lundquist, R. T. and Cais, M.,  
ULTRAVIOLET SPECTRA OF ORGANOMETALLIC COM-  
POUNDS, Journal of Organic Chemistry, Vol. 27, 1962,  
pp. 1167-1172.

Evidence was presented for the existence of electronic absorption bands typical of the transition metal-C bond. This evidence was based on a correlative qualitative study of the ultraviolet spectra of organo derivatives of Fe, Mn, Cr, and Mo. The characteristic features of these spectra were described. The following groups of compounds were examined: metallocarbonyls, substituted metallocarbonyls (sigma-bonded) substituted metallocarbonyls (pi-bonded), alkyl substituted ferrocenes, and phenyl substituted ferrocenes. Absorption spectra between 214 mμ and 700 mμ were obtained using 95 percent alcohol solutions. Appropriate dilutions were made to obtain transmittances in the range 10 to 80 percent. The molar extinction coefficients and their logarithms were determined at intervals of 4 mμ. The ultraviolet spectra curves were given for (1,3-butadiene) iron tricarbonyl, iron pentacarbonyl, chromium hexacarbonyl, manganese pentacarbonyl dimer, methylmanganese pentacarbonyl, (trifluoromethyl) manganese pentacarbonyl, acetylmanganese pentacarbonyl, (trifluoroacetyl) manganese pentacarbonyl, cyclopentadienylmanganese tricarbonyl, (methylcyclopentadienyl) manganese tricarbonyl, (acetylcyclopentadienyl) manganese tricarbonyl, (benzoylcyclopentadienyl) manganese tricarbonyl, cyclopentadienylmanganese tricarbonyl, [(methylsulfonyl) cyclopentadienyl] manganese tricarbonyl, [(chlorosulfonyl) cyclopentadienyl] manganese tricarbonyl, [(p-tolylsulfamoyl) cyclopentadienyl] manganese tricarbonyl, (sulfamoyl) cyclopentadienyl) manganese tricarbonyl, benzene-chromium tricarbonyl, mesitylenechromium tricarbonyl, anilinechromium tricarbonyl, N,N-dimethylanilinechromium tricarbonyl, mesitylenemolybdenum tricarbonyl, mesitylenechromium tricarbonyl, cyclopentadienyl (formylcyclopentadienyl) iron, cyclopentadienyl (acetylcyclopentadienyl) iron, cyclopentadienyl (carboxycyclopentadienyl) iron, dicyclopentadienyl iron, cyclopentadienyl (phenylcyclopentadienyl) iron, cyclopentadienyl [(p-nitrophenyl) cyclopentadienyl] iron, cyclopentadienyl [(p-ethoxycarbonylphenyl) cyclopentadienyl] iron, bis (phenylcyclopentadienyl) iron bis[ (α,α-dimethylbenzyl) cyclopentadienyl] iron, bis(benzylcyclopentadienyl) iron, bis(1,3-diphenylcyclopentadienyl) iron, and bi (1,2,4-triphenylcyclopentadienyl) iron.

526. Martin, D. H. and Stone, C. D.,  
RELAXATION OF FERROELECTRIC PHOSPHATES (ADP  
AND KDP) IN THE EXTREME INFRARED, Physics Letters,  
Vol. 5, 1963, pp. 26-27.

The reflectivities at 45° incidence of pressed-powder samples of  $\text{NH}_4\text{H}_2\text{PO}_4$  and  $\text{KH}_2\text{PO}_4$  at 34, 51, and 120  $\text{cm}^{-1}$  in the region of 80 to 260°K. showed a marked change at the Curie points, where the reflectivity decreased strongly with increasing frequency. This was attributed to a relaxation mechanism. Resonant contributions, if present, are heavily damped.

527. Pavlik, I. and Plechacek, V.,  
UBER DAS IR-SPEKTRUM VON DEUTERIERTEM  
FERRICINIUM, Collection of Czechoslovak Chemical  
Communications, Vol. 31, No. 5, 1966, p. 2083.

Within the framework of oscillation spectrum studies of the ferricinium cation, we investigated the infrared spectrum of the ferricinium - d - 10 cation. The IR-absorption bands were contributed to the infrared active fundamental oscillations. The validity of the assumption was tested by calculating the deuterium factors of the specific oscillations and with the aid of the Teller-Redlich product for oscillations of the same type of symmetry. At the same time we defined several fundamental frequencies of the oscillations, and found significant qualitative differences in the intensities of the absorption bands of specific fundamental oscillations between ferrocene and ferricinium - d - 10 spectrum verified the earlier findings that due to different formation conditions the frequency of several fundamental oscillations of the cation are displaced, in comparison to the frequencies of the same oscillations in the neutral molecule.

528. Pavlik, I. and Zizek, V.,  
ACETYLFERRICINIUM SALTS, Collection of Czechoslovak  
Chemical Communications, Vol. 31, No. 5, 1966, p. 1985.

Acetylferricinium salts (tetrachloroferrate, reinckate, and tungstosilicate) were prepared for the first time by oxidizing acetylferrocene. The presence of acetylferricinium was confirmed by chromatographic analysis of the products of the reduction of the salts and the infrared spectra which contain the characteristic absorption bands of ferricinium and of

the acetyl group. Some fundamental frequencies of the ferricinium nucleus of acetylferricinium are shifted against acetylferrocene, in a similar way as the corresponding frequencies of ferricinium against ferrocene. The blue shift of the frequency  $\nu(\text{C}=\text{O})$  and the red shift of  $\nu(\text{C}_{\text{ring}} - \text{C}_{\text{acetyl}})$  shows that the carbonyl group of the acetyl in acetylferricinium is less conjugated with the ferricinium nucleus than in acetylferrocene with the ferrocene nucleus.

529. Smith, F. J.,  
STUDIES IN MOLECULAR SPECTROSCOPY, I. EXCIMER FLUORESCENCE, II. HEAVY-ATOM SPIN-ORBITAL COUPLING EFFECT, AND III. THE ELECTRONIC SPECTRA OF FERROCENE, University Abstracts (Ann Arbor, Michigan) Order No. 66-748 115 pp., Dissertation Abstracts, Vol. 26, No. 8, 1966, p. 4274.

Refer to item No. 82 for abstract.

530. Wyandotte Chemicals Corporation, Michigan,  
SYNTHESIS OF METAL-CYCLOPENTADIENYL DERIVATIVES FOR USE AS ULTRAVIOLET ABSORBERS by R. L. Schaaf, and K. L. Rinehart, Jr., April 1962, Report No. TR61 108 P2, AD-283 843, Contract No. AF33 616 7214 (Unclassified Report).

In a program toward synthesis of metal cyclopentadienyl compounds as additives, monomers, and polymers with high UV radiation resistance, 13 candidate ferrocenes were prepared, and the spectral characteristics in the 2000 to 5000 angstrom region were obtained. Additives prepared were 1,1'-bis(B-fluorobenzoyl)-ferrocene, phenyl ferrocenoate, 1,1'-dibutylferrocene, 2-carboxybenzoylferrocene, benzoylferrocene oxime, 1,1'-bis(alpha-hydroxyethyl)-ferrocene, osmocene, and benzoylosmocene. Monomers synthesized were 1,1'-ferrocene diisocyanate, bis(2,3-epoxypropyl) 1,1'-ferrocenedicarboxylate, 1,1'-bis(n-methyl-n-(p-aminophenyl)-carboxamido)-ferrocene, dimethyl 1,1'-ferrocenedicarboxylate and 1,1'-di(hydroxymethyl)-ferrocene. 1,1'-diacetylferrocene reacted with benzene diazonium chloride to give 6-methyl-6-hydroxy-2-phenylazofulvene. Acetylation of acetamidoferrocene gave 1'-acetyl-1-acetamidoferrocene. The ratios of isomers formed in acetylation of mono- and di-bridged ferrocenes were measured accurately. 1,1'-diacetamidoferrocene and a tri-bridge ferrocene were prepared.

531. Wyandotte Chemicals Corporation, Michigan,  
SYNTHESIS OF METAL-CYCLOPENTADIENYL DERIVATIVES  
FOR USE AS ULTRAVIOLET ABSORBERS by R. L. Schaaf  
and K. L. Rinehart, Jr., May 1961, Report No. TR61 108,  
AD-268 773, Contract No. AF33 616 7214 (Unclassified Report).

In a search for ferrocene derivatives that may be useful as protective ultraviolet absorbers, twelve candidate ferrocenes were synthesized, the spectral characteristics in the 2000 to 5000 Å region were obtained, and the melting points, micro boiling points, and solubility properties of the ferrocenes were determined. Thus, 2-methoxybenzoylferrocene, 2,4-dimethoxybenzoylferrocene, benzoylferrocene, 1,1'-dibenzoylferrocene, and diferrocenyl ketone were prepared by Friedel-Crafts reactions on ferrocene. The methoxy compounds were converted to 2-hydroxybenzoylferrocene, 2,4-dihydroxybenzoylferrocene, and 2-hydroxy-4-methoxybenzoylferrocene by treatment with aluminum chloride. Ethyl ferrocenemonocarboxylate and diethyl 1,1'-ferrocenedicarboxylate were prepared from the crude acids, and basic hydrolyses of these esters furnished pure ferrocenemonocarboxylic acid and 1-carboxy-1'-carbethoxyferrocene. At 345°C, ferrocenemonocarboxylic acid decomposed to pure ferrous ferrocenemonocarboxylate.

532. Yavorskii, B. M., Kochetkova, N. S., Zaslavskaya, G. B.,  
and Nesmeyanov, A. N.,  
ABSORPTION SPECTRA OF SOME FERROCENE DERIVATIVES,  
Doklady Akademii Nauk SSSR, Vol. 149, 1963, pp. 111-113.

The following absorption maximum (and the spectra) are reported for the indicated ferrocenes (first maximum, inflection, second maximum, given, respectively, in mμ): ferrocene 440, -, 325; acetylferrocene 446, 356, 319; propionylferrocene 446, 356, 319; butyrylferrocene 446, 356, 319; 1,1'-diacetylferrocene 455, 355, 318; 1,1'-dipropionylferrocene 455, 355, 318; 1,1'-dibutyrylferrocene 455, 355, 318. The following maximums are also reported: ethylferrocene 438.5, 325; propylferrocene 438.5, 325; 1,1'-diethylferrocene 437, 325; 1,1'-dipropylferrocene 437, 325.

533. Yavorskii, B. M., Zaslavskaya, G. B., Kochetkova, N. S., and Nesmeyanov, A. N.,  
ABSORPTION SPECTRA OF SOME FERROCENE DERIVATIVES,  
Tr. Komis. po Spektroskopii, Akademii Nauk SSSR, Vol. 3,  
No. 1, 1964, pp. 350-354 (In Russian).

Absorption spectra of ferrocene and its alkyl and acyl derivatives were studied, 180-300 m $\mu$ ; absorption spectra of carboxylic acids of ferrocene and their esters were studied, 180-700 m $\mu$ . All compounds had maximums at 200-230 m $\mu$ . Oscillator forces were calculated for all studied absorption bands. Previous conclusions on band position and principles of band displacement were confirmed.

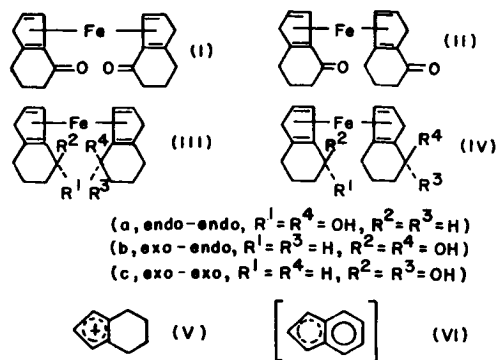
#### E. Mass Spectroscopy

534. Clancy, D. J. and Spilners, I. J.,  
ANALYSIS OF FERROCENES BY MASS SPECTROMETRY,  
Analytical Chemistry, Vol. 34, 1962, p. 1839.

Mass spectra of ferrocene and substituted ferrocenes were obtained at an ionizing voltage of 8 e.v. In all cases intense molecular ion peaks were produced with little or no fragmentation. Observed intensities, in units of chart divisions, for the molecular ions ranged from 222 for biferrocenyl to 3740 for dimethylethoxysilylferrocene. The intensities do not indicate the relative sensitivities of the compounds because unequal sample sizes were used in determining the spectra.

535. Egger, H. and Falk, H.,  
CONFIGURATION AND MASS SPECTRA OF ISOMERIC BIS  
( $\alpha$ -HYDROXYTETRAMETHYLENE) FERROCENE, Tetrahedron Letters, Vol. 4, 1966, pp. 437-444 (In German).

Reduction of bis( $\alpha$ -oxotetramethylene) ferrocene, both of the racemic (I) (carmine-red, m. 160°) and of the meso (II) (orange-red, m. 170°) forms, yielded six diols, of which IIIa (m. 158-61°), IIIb (m. 132-40°), IVa (m. 144-6°), and IVb (m. 122-4°), were isolated by thin-layer chromatography. The mass spectra of the endo- and exo-compounds (IIIa/IIIb and IVa/IVb) are characteristically different. The endo-endo compounds do not lose H<sub>2</sub>O molecules as easily as the exo-endo compounds. Furthermore, they have a high-intensity 118 peak, corresponding to fragment V. It is formed by splitting of a cyclopentadienyliron ring and the simultaneous transfer of



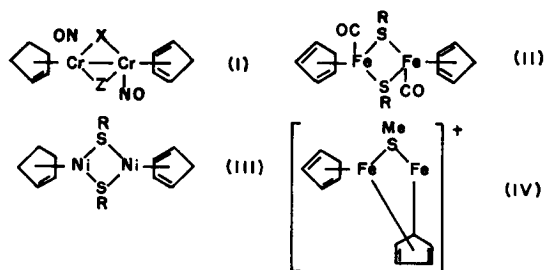
an OH group, bound by an Fe-H bridge, to Fe. The 117-115 pair originates by simple Fe-ring splitting, dehydration (117), and subsequent dehydrogenation (115, system VI). More surprising are the differences between the compounds relative to their origin (IIIa/IVa and IIIb/IVb). The splitting of a first H<sub>2</sub>O molecule is easier and that of a second H<sub>2</sub>O molecule is more difficult with the compounds coming from the racemic form. This is explained by the possibility of intramolecular ether formation, which is sterically impossible with the meso form. This behavior is not so unexpected when comparing the other physical and chemical properties. Ir spectroscopy shows that IIIa form very strong intermolecular associates, whereas IVa forms intermolecular bridges only at the normal conclusions.

536. Mandelbaum, A. and Cais, M.,  
 ORGANOMETALLIC STUDIES. XI. MASS SPECTROMETRY.  
 1. FRAGMENTATION OF SOME SUBSTITUTED FERROCENES  
 UNDER ELECTRON IMPACT, Tetrahedron Letters, Vol. 51,  
 1964, pp. 3847-3852.

The mass spectra of C<sub>5</sub>H<sub>5</sub>FeC<sub>5</sub>H<sub>4</sub>COR (R = Me, Ph, p-MeOC<sub>6</sub>H<sub>4</sub>, OH, OD, OMe, and NHMe) indicated that fragmentation led to loss of a 56-mass unit corresponding to the Fe atom in contradiction to a literature report.

537. Preston, F. J. and Reed, R. L.,  
 MASS-SPECTRAL STUDIES OF BINUCLEAR METAL  
 COMPLEXES, Chemistry Communications, Vol. 2, 1966,  
 pp. 51-52.

Mass spectra of the Cr compounds (I) (where X = Z = SMe; X = Z = SPh; X = SMe; Z = OH; X = Z = OMe; X = Z = NMe<sub>2</sub>) all show the ion m/e 182 which must be [chromocene]<sup>+</sup>. The Fe and Ni compounds (II and III), where R = Me or Ph, show dissociation through an intermediate of



type IV. The metallocenes observed in the latter spectra are probably formed by thermal processes.

#### F. Conductivity Measurements

538. Army Electronics Laboratory, Fort Monmouth, New Jersey,  
 MEASUREMENTS OF TRUE DARK CONDUCTIVITIES IN  
 FERROCENE CRYSTALS by E. Zehler and C. L. Burke,  
In Army Scientific Conference Proceedings, Vol. 11, 1965  
 N65-22314 (Unclassified Report).

Systematic dark conductivity measurements made on ferrocene crystals are reported. This material was chosen because of its low room temperature resistivity of the order of  $10^{13}$  ohm cm and its simple structure. The resistivity was found to follow an experimental dependence on temperature. The spread of resistivity was large extending over three orders of magnitude at room temperature. The thermoelastic power was measured on crystals about  $0.5 \text{ cm}^2$  and about 0.4 mm thick, drawn by either sublimation or from benzene solution. As a result of experiments which included voltage probing along the crystal, long time observations, and resistivity measurements, it was concluded that contact and surface



effects, and dielectric relaxation effects had a negligible effect on the conductivity of ferrocene crystals providing sufficient time is allowed for the measurements. A true dark conductivity was found to exist in ferrocene which varied from sample to sample and from  $10^{-12}$  to  $10^{-14}$  ohm<sup>-1</sup> cm<sup>-1</sup> with no apparent dependence on impurities or crystal direction.

539. Army Signal Research and Development Agency and Laboratory, Fort Monmouth, New Jersey, MEASUREMENTS OF TRUE DARK CONDUCTIVITIES IN FERROCENE CRYSTALS by E. Zehler and C. Loscoe, May 1964, Report No. TR-2459; AD-603815, N64-30581 (Unclassified Report).

This report describes systematic dark conductivity measurements on a monomeric organic crystal. The material chosen is ferrocene, a metalloorganic compound, and single crystals were grown from solutions or the melt by the Bridgman technique. Because of its relatively low room-temperature resistivity of the order  $10^{13}$  ohm cm and simple structure, the material appears to be very suitable as a model substance for dark conductivity investigations. From the measurements performed, including four-probe measurements, voltage probing between contacts, guard ring methods, and long-time observations, it can definitely be established that contact effects and dielectric relaxation have a minor effect on the resistance of the sample, provided sufficient time is allowed for the observation, and that a true dark conductivity and activation energy can be determined within a few percent accuracy.

540. Loscoe, C., DEPENDENCE OF THE ELECTRICAL RESISTIVITY OF FERROCENE SINGLE CRYSTALS ON DISLOCATIONS, 1965, 11 pp. AD622496.

Etch pits were obtained on the surfaces of ferrocene single crystals, which were grown from a solution of benzene and ferrocene by two methods: simple evaporation in air, and etching in MeOH. For each sample, the etch pit d. (N), which indicates the number of dislocations in the crystals, was determined on the (001) surface of the crystals, and the resistivity was measured in a direction perpendicular to this face. The resistivity is greater for samples with greater etch pit d., and may be expressed as resistivity =  $3.3 AN$ , where A is a constant.

541. New York University, School of Engineering and Science, New York,

APPLICATION OF ULTRA HIGH PRESSURE TO A STUDY OF ORGANIC SEMICONDUCTORS FINAL REPORT FOR 1 MARCH 63 - 28 FEBRUARY 65 by Y. Okamoto, 3 June 1965, Report No. AFCRL 65-294, AD-620 938, Contract No. AF19 628 2482 (Unclassified Report).

The electrical conductivity measurement apparatuses for organic compounds under the pressure range of 1 to 40,000 atmospheres and at various temperatures (25° to 400°C) were developed. The effects of pressure and temperature on the electrical conductivity of organic compounds such as ferrocene, nickelocene, tetrathiotetracene-o-chloranil, cobaltocene 3, 3', 5, 5' tetrabromo p-diphenoquinone and durene diaminechloranil complexes were investigated. The effect of pressure on the electrical properties of the organic solids is discussed. Some theoretical considerations on the effects of the structure of organic compounds were made. The infrared spectrum measurement of organic compounds under pressure was also studied. The results indicated the molecule became closed together and bonding charge transfer complexes tended to form dative bonding. Compressibility and single crystal growth of organic compounds with heating under pressure were attempted.

**G. Mössbauer Spectroscopy, Polarography, Microanalytical Techniques, and Other Analytical Procedures**

542. Bohn, R. K. and Haaland, A.,  
STRUCTURE OF FERROCENE, Journal of Organometallic Chemistry, Vol. 5, 1966, pp. 470-476.

Electron diffraction studies of ferrocene vapor at 140° show that the free molecule has an eclipsed ( $D_{5h}$ ) equilibrium configuration with a small barrier to internal rotation. The barrier is estimated to be about 1.1 kcal/mole. The principal molecular parameters are: C-C,  $1.431 \pm 0.005$  Å; Fe-C,  $2.058 \pm 0.005$  Å, and C-H,  $1.122 \pm 0.020$  Å. The C-H bonds seem to be bent about 5° out of the plane of the  $C_5$  ring towards the iron atom.

543. Collins, R. L.,

MÖSSBAUER STUDIES OF IRON ORGANOMETALLIC COMPLEXES. IV. SIGN OF THE ELECTRIC-FIELD GRADIENT IN FERROCENE, Journal of Chemical Physics, Vol. 42, 1965, p. 1072.

The quadrupole splitting of  $^{57}\text{Fe}$  Mössbauer spectra gives the magnitude, but not the sign, of the electric-field gradient. The sign can be determined by magnetically perturbing the energy levels, such that one line splits into a triplet and the other line splits into a doublet. A first order perturbation treatment for the axially symmetric electric-field gradient case is given for powdered samples. The method is applied to ferrocene, which has been the subject of many theoretical papers. A crystal-field treatment predicts a positive efg, and molecular orbital treatments predict negative efg's. At 40 kG applied, the two lines split clearly into a doublet and a triplet. The result agrees with the MO treatment. This also explains the essential vanishing of the efg in ferrocenium compounds.

544. Hartley, A. M. and Visco, R. E.,

POLAROGRAPHY OF NITROFERROCENE, Analytical Chemistry, Vol. 35, No. 12, 1963, pp. 1871-1874.

The aromatic character of nitroferrocene (I) was studied. Polarographic reduction in buffered (pH 4-9) 25 volume percent aqueous. EtOH showed only one wave, which was diffusion controlled. Although the process was definitely irreversible, the half-wave potential,  $E_{1/2}$ , shifted 58 mv./pH unit. The overall process involved six electrons, as shown by the ratio of the diffusion current constant for the reduction of I to that for the oxidation of ferrocene, both in 50 percent EtOH. Electrochemistry reduction of I in an electron spin resonance spectrometer gave an unstable radical with a N coupling constant of 15.1 gauss. In aqueous buffers I underwent photochemical decomposition and yielded a second polarographic wave with  $E_{1/2}$  identical to that of the Na salt of 1-nitrocyclopentadiene.

545. Jenik, J. and Renger, F.,  
ANALYSIS OF ORGANOMETALLIC SANDWICH COMPOUNDS,  
III. SIMULTANEOUS MICRODETERMINATION OF IRON AND  
TITANIUM IN DONOR-ACCEPTOR COMPLEXES OF FERRO-  
CENE BASES, Collection of Czechoslovak Chemical Communi-  
cations, Vol. 29, No. 9, 1964, pp. 2237-2239 (In German).

Dissolve two to four mg. of the sample in two ml. of 0.1N HNO<sub>3</sub> and two ml. HOAc. After 15 min. boil briefly with two ml. saturated aqueous Br. Add five ml. M NaOAc and two ml. HOAc, and remove excess Br with a few drops of formic acid. Add two to three mg. of sulfosalicylic acid and determine Fe by titrating with 0.005 M EDTA. In the same solution determine Ti after addition of two g. of crystallized NaOAc and 10 ml. of 0.02 M EDTA. Make alkaline with NH<sub>3</sub> buffer to phenolphthalein and extract four times with 10 ml. of one percent 8-hydroxyquinoline solution in CHCl<sub>3</sub>. Dilute to 50 ml. with EtOH and measure the absorbance at 450 mμ. The standard deviation of two determinations is <0.3.

546. Komenda, J. and Tirouflet, J.,  
OSCILLOPLOAROGRAPHY AND STRUCTURAL INFLUENCES  
IN THE FERROCENE SERIES, Comptes Rendus, Vol. 254,  
1962, pp. 3093-3095.

Oscillopolarograms of curves of  $dE/dt = f(E)$  were made at equilibrium conditions on compounds in the ferrocene series in dilute alcohol solutions (50 percent ethanol, MHClO<sub>4</sub>) containing  $5 \times 10^{-3}$  MX-substituted ferrocene. The method of using the Hg dropping electrode showed that the reaction is reversible no matter what X was. A linear correlation exists between the potential  $\Delta Q(X)$  and  $\sigma_p(X)$  and does not exist when one uses  $\sigma_m$  or  $\sigma$ . Some compounds where X is CH:NOH, CMe:NOH, and NH<sub>2</sub> vary to the right of the linear correlation because of the manner of determination of  $\sigma$ .  $\sigma$  is excited by the conjugation between the center of reaction and the substituent in the reaction NO<sub>2</sub> → NHOH. A like excitation occurs when the center of reaction is an atom of Fe. The ferrocene series may be extrapolated to the benzene series and this enlarged the method of determination of  $\sigma_p$ . H bonding in certain carbonyls between carbonyl and N may appreciably attenuate  $\Delta Q$ .

547. Lesikar, A. V.,  
EFFECT OF A SUBSTITUENT ON THE  $^{57}\text{Fe}$  MOESSBAUER  
SPECTRUM OF CERTAIN FERROCENE DERIVATIVES,  
Journal of Chemical Physics, Vol. 40, No. 9, 1964, pp. 2746-  
2747.

Moessbauer effect data were given for ferrocene, methylferrocene, ferrocenylcarbinol, cyanoferrocene, palmitoylferrocene, acetylferrocene, 1,1'-ditridecanoylferrocene, ferrocenylpropionic acid, 1,1'-dicaprylylferrocene, 1,1'-diacetylferrocene, 2-acetyl- 1,1'-trimethyleneferrocene, 1,1'-trimethyleneferrocene,  $\text{FeEt}_2\text{-(MeCH)}_2\text{O}$ , biferrocenyl, diferrocenylmercury, and chloromercuriferrocene. There was a small decrease in the quadrupole coupling in the substituted ferrocenes from the value of this coupling in the unsubstituted ferrocene. The isomeric shift varied only slightly through the derivatives.

548. Myshlyaeva, L. V., Krasnoshchekov, V. V., Shatunova, T. G., and Sedova, I. V.,  
IRON DETERMINATION IN FERROCENE AND ITS SILICON-ORGANIC DERIVATIVES, Tr. Mosk. Khim. - Teknol. Inst., No. 49, 1965, pp. 178-180 (In Russian).

To determine Fe in title compounds, dissolve 0.05 g. of sample in 10 ml.  $\text{CCl}_4$ , add 10-15 ml. concentrated HCl and ~one g.  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ , warm while stirring till the color changes from blue to yellow, and boil the resulting solution until no Cl is evolved. Then titrate either iodometrically or with EDTA (sulfosalicylic acid as an indicator) by standard procedures. The absolute error of the method was from -0.20 to +0.25 percent Fe (Fe content 18.05 to 42.93 percent).

549. Peterlik, M. and Schlogel, K.,  
FERROCENE DERIVATIVES. XIV. MOLECULAR-WEIGHT DETERMINATION OF FERROCENE DERIVATIVES VIA POTENTIOMETRIC TITRATION WITH DICHROMATE, Zhurnal of Analytical Chemistry, Vol. 195, 1963, pp. 113-117.

Ferrocene derivatives undergo a one-electron change on direct potentiometric titration in aqueous HOAc with  $\text{K}_2\text{Cr}_2\text{O}_7$  and Pt-calomel electrodes. The equivalent weight determination is therefore a molecular weight determination. Acyl ferrocenes are reduced with  $\text{LiAlH}_4\text{-AlCl}_3$  to alkyl ferrocenes first. The following ferrocenes were analyzed: ethyl-, amyl-, benzyl-,

$\alpha$ -thenyl-,  $\alpha$ -naphthyl-, hydroxymethyl-, 1-hydroxy-2,2-dichloroethyl-, 1,1'-trimethylene-, 1,1'-di-Et-, 1,1'-diamyl-, and 1,1'-bis( $\alpha$ -hydroxybenzyl-). Diferrocenylmethane,  $\alpha,\alpha'$ -di-ferrocenydimethyl ether, 3-ferrocenylpyrazole, and 3-Me-5-Et-5-ferrocenylhydantoin were also measured.

550. Royal Aircraft Establishment, Farnborough, Great Britian, SUB-MICRO ANALYSIS. II. THE DETERMINATION OF IRON IN ORGANIC MATERIALS by T. R. F. W. Fennell and J. R. Webb, June 1962, Report No. RAE-TN-CHEM-1396 X62-11010 (Unclassified Report).

A submicromethod for the determination of iron in solid organic compounds such as ferrocene and its derivatives has been developed. Sample weights between 25 and 400  $\mu\text{g}$  were used, the optimum sample size being such as to contain between 10 and 20  $\mu\text{g}$  of iron. Results obtained from the analysis of standard compounds have all been within  $\pm 0.5$  percent absolute. An indication is given of the utility of working on the small scale in detecting inhomogeneity of samples.

551. Texas University, Department of Physics, Austin, Texas, MÖSSBAUER STUDIES OF IRON ORGANOMETALLIC COMPLEXES. IV. SIGN OF THE ELECTRIC FIELD GRADIENT IN FERROCENE by R. L. Collins, AD-617 523 (Unclassified Report).

The quadrupole splitting of  $^{57}\text{Fe}$  Mössbauer spectra gives the magnitude, but not the sign, of the electric field gradient. The sign can be determined by magnetically perturbing the energy levels, such that one line splits into a triplet and the other line splits into a doublet. A first-order perturbation treatment for the axially symmetric electric field gradient case is given for powdered samples. The method is applied to ferrocene, which has been the subject of many theoretical papers. A crystal field treatment predicts a positive E. F. G., and molecular orbital treatments predict negative E. F. G.'s. At 40 kilogauss applied, the two lines split clearly into a doublet and a triplet. The result agrees with the M. O. treatment. This also explains the essential vanishing of the E. F. G. in ferrocinium compounds.

552. Tirouflet, J., Dabard, R., and Laviron, E.,  
 STUDIES IN METALLOCENE SERIES. III. POLAROGRAPHY  
 OF FUNCTIONAL GROUPS IN (SUBSTITUTED) FERROCENES  
 AND CYCLOPENTADIENYL-MANGANESE TRICARBONYLS,  
Bulletin Société Chimique de France, Vol. 8-9, 1963, pp. 1655-  
 1660.

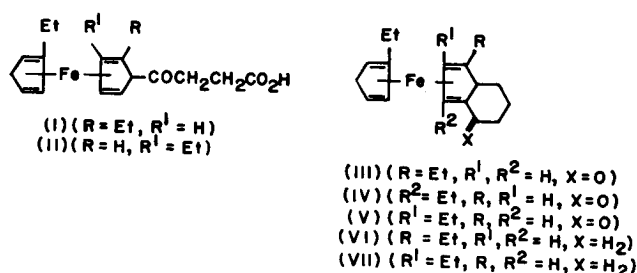
The Friedel-Crafts synthesis of some ferroceno ketones,  $\text{FcCOR}$  (I) and their oximes described (R given):  $\text{CH}_2\text{Ph}$ , m.  $130^\circ$  (oxime m.  $150^\circ$ );  $o\text{-C}_4\text{H}_4\text{Me}$ , b<sub>1.5</sub>  $130.5^\circ$ ;  $p\text{-C}_5\text{H}_4\text{Me}$ , m.  $132^\circ$ ; furyl, m.  $80^\circ$ ; thienyl, m.  $125^\circ$  (oxime m.  $138^\circ$ ); pyridyl, m.  $163^\circ$ . Also separated was ferroceno-1,2-cyclohexanone 3-oxime, m.  $140\text{-}1^\circ$ . By similar methods cyclopentadienylmanganese tricarbonyl ketones,  $\text{CMTCOR}$ , were prepared (R given):  $\text{CH}_2\text{Ph}$ , m.  $60^\circ$ ,  $\text{C}_6\text{H}_4\text{Me}$ , m.  $180^\circ$ ;  $p\text{-C}_6\text{H}_4\text{Me}$ , m.  $95^\circ$ ; furyl, m.  $78^\circ$ ; thienyl, m.  $114^\circ$ . The half-wave potentials ( $E_{1/2}$ ) of these and other substituted ferrocene compounds ( $10^{-3}$  M solutions) were measured polarographically in  $\text{H}_2\text{O}$ - $\text{EtOH}$  (40 percent  $\text{EtOH}$ ) at  $25^\circ$  and the values compared with the analogous benzene substituted derivatives. The tabulated results show the ferrocene radical to be more electropositive than the Ph radical and in the ketone series, the values for the first  $E_{1/2}$  are in the order  $\text{CMTCOR} \leq \text{PhCOR} < \text{FcCOR}$ . Two steps appear in the polarograms of the  $\text{CMTCOR}$  compounds due to the reactions shown. Variation of the substituent in



the ferroceno ketone,  $\text{FcCH:CHCOR}$ , series, varies the  $E_{1/2}$  in the order  $\text{R} = 2\text{-pyridyl} < \text{phenyl} \leq \text{thienyl} < \text{ferrocenyl} \leq 2\text{-pyrrolyl}$  and the  $E_{1/2}$  value is approximately linearly dependent on the pH in the range 2 to 13. Mono and disubstituted acyl ferrocene derivatives are easily distinguished by their oscillographic polarograms.

553. Tirouflet, J., Tainturier, G., and Dabard, R.,  
 METALLOCENES. IV. A GENERAL METHOD FOR THE  
 IDENTIFICATION OF POLYSUBSTITUTED FERROCENES,  
Bulletin Société Chimique de France, Vol. 10, 1963, pp. 2403-  
 2405.

The two succinoylation products of 1,1'-diethylferrocene, I, m. 54°, and II, m. 52°, were identified by determining the number of possible ring closures (one or two, respectively). I gave, via Clemmensen reduction and polyphosphoric acid condensation, solely III, m. 39°. Similarly, II gave a mixture of IV, b<sub>3</sub> 179-84° (oxime m. 68°), and V, b<sub>3</sub> 187° (oxime m. 76°). IV and



V were separated in C<sub>6</sub>H<sub>6</sub> on an Al<sub>2</sub>O<sub>3</sub> column. Reduction of III and IV both led to VI, b<sub>5</sub> 60-70°. Similarly, V gave VII, b<sub>5</sub> 90-5°.

554. Toma, S.,  
 DERIVATIVES OF FERROCENE. XII. FERROCENE ANALOGS  
 OF CHALCONES, Chemické Zvesti, Vol. 19, No. 9, 1965,  
 pp. 703-710 (In Slovak).

By the aldol condensation of the acetylferrocenes or 1-acetyl-1'-benzoylferrocenes with aromatic aldehydes, ferrocene analogs of chalcones were prepared and determined by thin-layer chromatography and polarography. In the chalcones derived from the acetylferrocenes the halfwave potentials were plotted in the diagram against Hammett's  $\sigma$  constant. A linear relationship was determined as expressed in the equation:  $\Delta E_{1/2}^0 = +0.17 \sigma$ . In the chalcones derived from the 1-acetyl-1'-benzoylferrocenes, the values of halfwave potentials practically do not depend on the nature of the substituent. Analyses of 22 prepared compounds are given.



555. Wertheim, G. K. and Herber, R. H.,  
<sup>57</sup>Fe MOESSBAUER EFFECT IN FERROCENE DERIVATIVES,  
Journal of Chemical Physics, Vol. 38, 1963, pp. 2106-2611.

The hyperfine structure in the Moessbauer spectrum of <sup>57</sup>Fe in ferrocene and in related compounds shows that the bonding of the iron atom is not affected by ring substitution. The temperature dependence of the fraction of recoil-free absorption events in these compounds indicates that the Debye temperature is low (~150°K), and that the optical modes make only a minor contribution to the reduction of the recoil-free fraction at low temperature.

A. Propellant Additives

556. Auburn University, Auburn, Alabama,  
A STUDY OF THE DECOMPOSITION MECHANISM OF  
AMMONIUM PERCHLORATE, 1 JANUARY - 1 APRIL 1965,  
April 1965, Report No. 4, AD-463 772, Contract No. DA-01-  
009-ORD-1023 (Z) (Unclassified Report).

Differential thermal analysis runs were made at various heating rates on ammonium perchlorate samples to which various additives were added for determining the catalytic effect of the additives. A total of 68 such determinations were conducted. The synthesis of chemicals to be used in the determination of catalytic effects included hexammine iron (II) perchlorate, tetrapyridine iron (II) perchlorate, tetrammine zinc perchlorate, anhydrous zinc perchlorate and tetrammine cadmium perchlorate. Tabular listing gives the peak temperatures for the differential thermal analysis runs on ammonium perchlorate with various additives. The peak temperatures represent endotherm and exotherm peak temperatures as they occurred on the differential thermal analysis plot reading from low to high temperatures.

557. Auburn University, Auburn, Alabama,  
A STUDY OF THE DECOMPOSITION MECHANISM OF  
AMMONIUM PERCHLORATE, 1 OCTOBER - 31 DECEMBER  
1965 by J. E. Land, December 1965, Report No. 2,  
AD-626 805, Contract No. DA-01-021-AMC-12346 (Z)  
(Unclassified Report).

Efforts were concerned with: (1) A continuation of the making of differential thermal analysis runs at various heating rates on ammonium perchlorate samples to which had been added various metal oxides to measure the catalytic effect of these additives; (2) performing differential thermal analysis runs on ammonium perchlorate samples to which had been added certain metal complexes of the ferrocene type, and (3) beginning a series of differential thermal analysis runs on ammonium perchlorate samples which have been doped with a known percent of a metal perchlorate so as to determine the influence of this additive on the differential thermal analysis exotherms and endotherms recorded for ammonium perchlorate decomposition as it is heated at various rates over a given temperature range.

558. Battelle Memorial Institute, Columbus, Ohio,  
A STUDY OF SOLID-PROPELLANT VAPORIZATION AND  
DIFFUSION PROCESSES, FINAL TECHNICAL REPORT by  
J. W. Droege, R. W. King, J. S. McNulty, and A. Levy,  
31 August 1965, Report No. NASA-CR-68228, N66-12871,  
Contract No. NAS7-100, JPL-950813 (Unclassified Report).

The vaporization and diffusion processes for dioctyl adipate and ferrocene in a polyurethane propellant were studied in some detail; phenyl-beta-naphthylamine was studied in less detail. Vapor pressures of these three additives were measured. Diffusion studies were carried out on propellant samples containing dioctyl adipate and ferrocene. Measurements were made between 30 and 70°C. The diffusion coefficients found for these two materials were nearly the same. The vapor pressures differed by several orders of magnitude. Diffusion appeared to take place predominantly through the polymer phase. There were some indications of structure-dependent diffusion through cracks and boundaries between the binder and the oxidizer. If one assumes a rocket configuration in which the effective throat area is about  $3 \times 10^{-3}$  times the area of exposed propellant surface, then one concludes that at about 30°C the loss of dioctyl adipate will be controlled by its rate of effusion from the nozzle. Over a period of a few years, the loss would be negligible. For ferrocene, with a much higher vapor pressure, the loss is diffusion controlled and in a year would deplete the propellant considerably within a few millimeters of the surface, leaving the bulk of the propellant unaffected.

559. Rocketdyne, Canoga Park, California,  
PROPELLANTS FOR ELECTRICAL PROPULSION ENGINES  
OF THE CONTACT OR BOMBARDMENT ION TYPE by  
A. L. Cox and J. E. Colwell, Report No. TR61 151, AD-264  
784, Contract No., AF 33 616 7063 (Unclassified Report).

Spectrometers and Power Supplies. Research on the materials and methods for producing molecular and colloidal ion beams suitable for use in electrical propulsion devices is discussed. The substances under investigation for production of molecular ions were selected mainly on the basis of expected good ionization characteristics and high structural stability. The experimental techniques and results are described. Detailed drawings used for fabrication of a charged colloid generator based on the vapor-jet, rapid-condensation method

of colloid preparation with charging by electron bombardment before condensation are presented. The possibilities of using neutral assemblies of positive ions with negative or electrons as cold, collisionless plasma in JXB acceleration devices are discussed.

560. Rocketdyne, Canoga Park, California,  
PROPELLANTS FOR ELECTRICAL PROPULSION ENGINES  
OF THE CONTACT OR BOMBARDMENT ION TYPE by  
V. E. Bedwell and H. E. Dubb, Report No. TR61 150 P2,  
AD-293 913, Contract No. AF 33 616 7063 (Unclassified  
Report).

Materials and methods for producing molecular ions and a colloidal ion beam suitable for use in electrical propulsion devices are investigated. The molecular compounds were selected for study primarily on a basis of expected favorable ionization characteristics and high structural stability to fragmentation. A theoretical analysis of a colloid producing system which utilizes a convergent-divergent nozzle for rapid condensation of propellant is presented. Electrical charging of the droplets is accomplished by ionizing a fraction of the propellant vapor prior to expansion through the nozzle. A graphical approach for obtaining approximate thermodynamic conditions necessary to adiabatically condense propellant vapors in a typical colloid generating system is introduced. Experimental results from operation of a charged, mercury colloid generator are presented.

#### **B. Electrical Properties, Insulators, Dielectrics, etc.**

561. Army Electronics Command, Fort Monmouth, New Jersey,  
DEPENDENCE OF THE ELECTRICAL RESISTIVITY OF  
FERROCENE SINGLE CRYSTALS ON DISLOCATIONS by  
C. Loscoe, July 1965, Report No. ECOM-2619, AD-622 496,  
Contract No. DA-1P6 22001A056 (Unclassified Report).

Etch pits were obtained on the surfaces of ferrocene single crystals, which were grown from solution of benzene and ferrocene, by two methods: simple evaporation in air and, etching in methyl alcohol. For each sample, the etch pit density (N) which indicates the number of dislocations in

the crystals, was determined on the (001) surface of the crystals, and the resistivity was measured in a direction perpendicular to this face. The resistivity is found to be greater for samples with greater etch pit density, and may be expressed as resistivity =  $AN(3.3)$ , where A is a constant.

562. Army Electronics Command, Fort Monmouth, New Jersey, ELECTRONICALLY FUNCTIONAL ORGANIC MATERIALS by G. Platau, W. R. Wenger, and E. Beekman, September 1964, Report No. ECOM-2508, AD-609 831, Contract No. 1C0 24401A112, (Unclassified Report).

The syntheses of 14 compounds based on ferrocene, nickelocene, and cyclopentadiene are described. The infrared spectra for these compounds are shown. Conductivity and electron spin resonance absorption measurements performed on these and 12 other components obtained from external sources indicate poor electronic activity for most of these materials. The application of these compounds and organic compounds in general as active elements in electronic devices is discussed.

563. Army Electronics Laboratories, Fort Monmouth, New Jersey, MEASUREMENTS OF TRUE DARK CONDUCTIVITIES IN FERROCENE CRYSTALS by E. Zehler and C. Loscoe, May 1964, Report No. TR2459, AD-603 815, Contract No. 1G6 22001A056 04 22 (Unclassified Report).

The report describes systematic dark conductivity measurements on a monomeric organic crystal. The material chosen is ferrocene, a metallo-organic compound, and single crystals were grown from solutions or the melt by the Bridgman Technique. From the measurements performed, including four-probe measurements, voltage probing between contacts, guard ring methods, and long time observations, it can definitely be established that contact effects and dielectric relaxation have a minor effect on the resistance of the sample, provided sufficient time is allowed for the observation, and that a true dark conductivity and activation energy can be determined within a few percent accuracy. Furthermore, a slight anisotropy exists for the different crystal directions but the impurity content of the crystals does not significantly influence the conductivity, indicating an intrinsic type of conduction mechanism. These findings are supported by thermoelectric measurements on these materials which indicate that

holes are, at room temperature, more mobile than electrons. The implications of these data for establishing a model for the dark conductivity are discussed and recommendations made for further investigations.

564. Hughes Aircraft Company, Culver City, California, ORGANIC SEMICONDUCTOR STUDY by J. B. Rust, F. A. Haak, and J. P. Nolte, June 1960, Report No. TR60 111, AD-243 913, Contract No. AF33 616 6024 (Unclassified Report).

Not abstracted.

565. Naval Applied Science Laboratory, Brooklyn, New York, INVESTIGATION OF 1,1'-BIS (5-PHENYL-1, 1, 3, 3, 5-HEXAMETHYLTRISILOXANYL) -FERROCENE. ULTRA HIGH TEMPERATURE LIQUID DIELECTRIC MANUFACTURED BY WYANDOTTE CHEMICALS CORPORATION, WYANDOTTE, MICHIGAN by J. P. Randino, September 1961, Report No. 5940 P29, AD-264 415L (Unclassified Report).

An investigation was conducted to determine the electrical and physical properties of Wyandotte Chemical Corporation. 1, 1'-bis (5-phenyl-1, 1, 3, 3, 5, 5,-hexamethyltrisiloxanyl)-ferrocene liquid dielectric for use at temperatures up to 500° C. The results indicated decreasing dielectric breakdown characteristics as the temperature was increased to 415°C and poor 1 kilocycle dissipation factor characteristics at temperatures above 100°C. Thermogravimetric analysis showed liquid pyrolyzes rapidly in temperature range 250-415° C. Differential thermal analysis indicated the onset of exothermic changes at temperature as low as 255°C.

566. Naval Applied Science Laboratory, Brooklyn, New York, INVESTIGATION OF 1-PHENYLDIMETHYLSILYL-1'-(3-PHENYL-TETRAMETHYLDISILOXANYL)-FERROCENE ULTRA HIGH TEMPERATURE LIQUID DIELECTRIC MANUFACTURED BY WYANDOTTE CHEMICAL CORPORATION, WYANDOTTE, MICHIGAN by J. P. Randino, September 1961, Report No. 5940 P24, AD-263 910L (Unclassified Report).

Electronic equipment, insulating materials, dielectrics are discussed. Electrical and physical property studies of 1-phenyldimethylsilyl-1'-(3-phenyletetramethyl-disiloxanyl)-ferrocene liquid dielectric for use at temperatures up to

500°C are reported. The results, in general, indicated poor flash and pour point characteristics. Dissipation factor and insulation resistance were adversely affected as temperature was increased, and dielectric breakdown was considerably lowered at temperatures of 200°C and above. The liquid, in addition, showed poor resistance to heating at temperatures of 300°C or higher while sealed under a nitrogen atmosphere. Aging at 300°C caused formation of solid particles in as short an interval as 1 hour. Differential thermal analysis showed exothermic changes occurring at temperatures as low as 210° C.

567. Paushkin, Y. M., Polak, L. S., Vishnyakova, T. P., Patalakh, I. I., and Machus, F. F.,  
NEW IRON-CONTAINING POLYMERS ON THE BASIS OF FERROCENE AND THEIR ELECTROPHYSICAL PROPERTIES (Foreign Title Not Available), Translated into English from Russian by the Foreign Technical Division, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, October 1964, Report No. TT64 773, 64 71689, AD-608 051 (Vysokomolekulyarnye Soedineniya, USSR, Vol. 6, No. 3, 1964, pp. 545-550)

Obtained by means of polyrecombination and condensation polymerization were 14 new polymers based on ferrocene and its derivatives, and their properties were studied. It is shown that the polymers obtained, which represent polyconjugate systems, possess polyconductor properties. Their specific electrical resistances lie in the interval from  $1 \times 10^{12}$  to  $1 \times 10^9$  cm/ohm, and the energy of activation in the interval from 0.3 to 1.74 EV (without desorption from the surface). An explanation is given of the role and the effect of the surface adsorption on the semiconductor properties of the polymer of 1, 1'-diacetyl-ferrocene. It is shown that the greater energies observed from the activation are brought about to some degree by the excitation of pielectrons from the valence zone into the zone of conductivity of the macromolecules and basically by the surface adsorption.

568. Plastics Laboratory, Princeton University, New Jersey,  
HIGH POLYMER RESEARCH by L. F. Rahm, AD-234 610  
(Unclassified Report).

Not abstracted.

569. Plastics Laboratory, Princeton University, New Jersey,  
HIGH POLYMER RESEARCH by L. F. Rahm, AD-266 090  
(Unclassified Report).

Not abstracted.

570. Royal Aircraft Establishment, Farnborough, England,  
FERROCENE POLYMERS. PART II. THE POTENTIALITIES  
OF 1, 1'-DIMETALOFERROCENES FOR THE SYNTHESIS OF  
HIGH-TEMPERATURE RESISTANT POLYMERS by W. A. Lee,  
AD-287 572 (Unclassified Report).

The various contributions to the basic position error of practical incidence vanes are briefly reviewed. The dynamic response of a windvane is shown to depend critically on the aerodynamic damping and viscous friction aging on the vane. The vane responds differently to incidences generated by gusts, aircraft plunging, and by aircraft rotary motion. Frequency response formulae and graphs are given to illustrate some typical cases.

571. School of Engineering and Science, New York University, New York,  
APPLICATION OF ULTRA HIGH PRESSURE TO A STUDY OF  
ORGANIC SEMICONDUCTORS, FINAL REPORT by Y. Okamoto,  
June 1965, Report No. AFRCL 65-294, AD-620 938, Contract No.  
AF19 628 2482 (Unclassified Report).

The electrical conductivity measurement apparatuses for organic compounds under the pressure range of 1 to 40,000 atmospheres and at various temperatures (25° - 400°C) were developed. The effects of pressure and temperature on the electrical conductivity of organic compounds such as ferrocene, nickelocene, tetrathiotetracene-o-chloranil, cobaltocene 3, 3', 5, 5'-tetrabromo p-diphenquinone, and durene diamine-chloranil complexes were investigated. The effect of pressure on the electrical properties of the organic solids is discussed. Some theoretical considerations on the effects of the structure of organic compounds were made. The infrared spectrum



measurement of organic compounds under pressure was also studied. The results indicated the molecule became closed together and bonding charge transfer complexes tended to form dative bonding. Compressibility and single crystal growth of organic compounds with heating under pressure were attempted.

572. Texas Instruments, Incorporated, Dallas, Texas,  
ORGANIC MATERIALS FOR ELECTRONIC APPLICATIONS,  
FINAL TECHNICAL REPORT by R. E. Johnson, Report No.  
TR65-59, AD-460 594, Contract No. AF33 615 1364 (Unclassified Report).

This research program covered two aspects of organic materials for electronic application:

- 1) Preparation of thin polymeric organic films by DC glow discharge and some possible applications of the film.
- 2) A study of electrical conduction mechanisms in metal-organic polymeric compounds and an attempt to correlate electrical properties with chemical structure.

**C. Products of High Temperature Stability, Radiation Stability,  
and Ultraviolet Absorbability**

573. Aeronautical Systems Division, Air Force Systems Command,  
Wright-Paterson Air Force Base, Ohio,  
EVALUATION OF BUNA-N (NBR) GASKETS IN PROTOTYPE  
APPLICATIONS UNDER GAMMA FLUX by J. A. Parker and  
D. Hale, Report No. TR59 661, AD-267 111 (Unclassified Report).

Qualitative and quantitative sealability tests were evaluated to test the theoretical prediction of the ability of certain acrylonitrilebutadiene rubber stocks a reasonable agreement between sealability coefficients was obtained from the seal tester and relative replacement times overdose range from  $2 \times 10^9$  to  $2 \times 10^{10}$  ergs/g C (one Roentgen = 87.7 ergs). Evaluation criteria for these compositions were established by application of the Bopp-Sisman relationship to observed changes in the elastic modulus previously reported. The effect of ferrocene as a potential anti-rad was investigated and found to improve the radiation resistance of these stocks. The apparatus described for determining sealability of gasket materials consists of a method of applying a load on the gasket, equipment for pressurizing one side of the gasket seal, and a method for measuring gas leakage.

574. Air Force Materials Laboratory, Air Force Systems, Wright-Patterson Air Force Base, Ohio,  
NEW CANDIDATE HIGH TEMPERATURE LUBRICANTS FOR  
ADVANCED AEROSPACE SYSTEMS, REPORT FOR 1 JUNE-  
30 NOVEMBER 1963 by R. E. Dolle, August 1964, Report No.  
TDR64 153, AD-449 716 (Unclassified Report).

Ten new candidate fluids of various classes were investigated for high temperature lubricant application. The basic physical, chemical, and antiwear characteristics of the new materials were determined by oxidation, corrosion, fourball wear, and other standard test methods. For comparison, similar data were obtained for a MIL-L-9236B trimethylolpropane (TMP) ester base stock, a polyphenylether (5P-4E) base fluid, and a super-refined mineral oil formulation. A cyclic phosphonitrile mixture, m-trifluoromethylphenoxy tri- and tetraphosphonitriles (10°F pour point, has demonstrated outstanding oxidative and antiwear properties compared with 5P-4E. The oxidative stability of 2-phenoxy-3-(5-nonyl) pyrazine and 2-n-heptyl-6-n-nonylpyrazine was much improved when formulated with phenyl alpha-naphthylamine and bis (p-phenoxyphenyl) diphenyltin.

575. American Cyanamid Company, Stamford, Connecticut,  
STUDIES ON THE PROTECTIVE ULTRAVIOLET ABSORBERS  
IN A SPACE ENVIRONMENT by R. G. Schmitt and R. C. Hirt,  
April 1962, Report No. TDR62 9, AD-275 038, Contract No.  
AF29 601 2561 (Unclassified Report).

The effectiveness of the ultraviolet absorbers in protecting organic coatings exposed to an extraterrestrial environment from photochemical degradation was studied. The change in solar absorptivity of the coatings was used as a measure of the degradation incurred; these data being obtained from the ultraviolet, visible and near-infrared absorption spectra of the polymers. Ultraviolet absorbers of the benzophenone and benzotriazole type used for terrestrial applications were considerably less effective in a space environment. This was attributed to the strong ultraviolet absorption of the polymers at the shorter wavelengths which competes with the absorber for the incident radiation. Certain benzoyl substituted ferrocene compounds were extremely effective in protecting many types of polymeric coatings. Improvement in the stability of the coatings by factors of 30 to 5000 were obtained.

576. American Oil Company, Whiting, Indiana,  
DEVELOPMENT OF GREASE LUBRICANTS FOR HIGH  
TEMPERATURE BALL AND ROLLER BEARINGS OF ELEC-  
TRICAL EQUIPMENT by A. C. Borg and K. R. Bunting,  
October 1960, Report No. TR60 557, AD-249 399, Contract  
No. AF33 616 6584 (Unclassified Report).

Not abstracted.

577. Babare, L. V., Nametkin, N. S., and Chernysheva, T. I.,  
METHOD OF OBTAINING ORGANOSILICON COMPOUNDS  
CONTAINING FERROCENYL RADICAL (Foreign Title Not  
Available), Translated into English from Russian by the  
Foreign Technology Division, Wright-Patterson Air Force  
Base, Ohio, June 1965, Report No. FTD-TT-65-465,  
65-63030, AD-619 426 (USSR Patent 165 718, Application  
No. 851651/23-4, 8 August 1963).

The invention involves a method of obtaining organosilicon compounds which contain a ferrocenyl radical which has the distinguishing feature that, for the purpose of obtaining compounds with heightened heat resistance, silylferrocenes which contain the bond Si-H are subjected to interaction with di-(vinylary-lalkyl)-disiloxane or di-(vinylalkylaryl)-silylbenzene with heating up to 180° to 200°C in the presence of platinohydrochloric acid as a catalyst.

578. Berlin, A. A. and Kostroma, T. V.,  
POLYMERS WITH CONJUGATED BONDS AND HETERO-  
ATOMS IN A CONJUGATED CHAIN (Foreign Title Not Avail-  
able). Translated into English from Russian by the Foreign  
Technology Division, Wright-Patterson Air Force Base,  
Ohio, April 1965, Report No. FTD-TT-64-126), 65-62243,  
AD-615 243 (Geterotsepye Vysokomolekulyarnye Soedineniya  
(Heterochain High Molecular Weight Compounds), Moscow,  
1963, pp. 53-58).

Salicyl derivatives of ferrocene were obtained that were never described before. Polymer chelate complexes were obtained of tetrasalicylates of ferrocene with copper, beryllium, bi- and tetravalent iron, aluminum and magnesium, and complex compounds and disalicyl ferrocene with silver and copper. The thermal stability of the complexes obtained was determined and it was shown that the greatest resistance to heat is possessed by complexes with beryllium, as well as with

mg and al, which stand heating up to 200°C without significant loss in weight. The least thermal stability was observed in the case of complexes with copper, which at 200°C in the course of five minutes, lose 30 percent of their weight. It was established that the complexes of salicylates of ferrocene, in contrast to the corresponding monomer products, possess considerably higher magnetic susceptibility and higher electrical conductivity.

579. Carlson, E. H.,  
OXIDATION-STABLE POLY (PHENYL ETHERS) FOR USE AS  
LUBRICANTS AND HYDRAULIC FLUIDS, Belgium Patent  
657880, 5 July 1965, Applied 2 January 1964, 14 pp.

Compositions containing a poly(phenyl ether) and 0.1-2 wt. percent arylferrocene, such as phenylferrocene, 3-biphenyl-ferrocene, phenylthioferrocene, phenoxyferrocene, m-(m-phenoxyphenoxy) phenoxyferrocene (I), or N-phenylferrocenecarboxamide, are prepared. They are stable to oxidation at  $> 287.8^\circ$ , and can be used as lubricants and hydraulic fluids; the ethers contain  $\geq 50$  percent meta ether linkages. Thus, a solution [viscosity ( $37.8^\circ$ ) 360.5 centistokes] of two wt. percent I ( $m. 74.5-5^\circ$ ) in 1,3-bis (m-phenoxyphenoxy) benzene is heated for 21 hours. at  $315.6^\circ$  to give a viscosity of 367.3 centistokes, variation 1.9 percent, as compared with 16.7 for the control.

580. Gulf Research and Development Company, Pittsburgh, Pennsylvania,  
DEVELOPMENT OF HIGH TEMPERATURE GREASE FOR  
HIGH SPEED BALL AND ROLLER BEARINGS, TECHNICAL  
DOCUMENTARY REPORT, 1 FEBRUARY 1963 - 31 JANUARY  
1964 by P. R. McCarthy, J. F. Hedenburg, E. R. Dzuna,  
C. S. Tempalski, and T. R. Orem, April 1964, Report No.  
ML-TDR-64-69, AD-451 637, X65-11929, Contract No.  
AF 33(657)-8048 (Unclassified Report).

Reported is the development of greases capable of lubricating antifriction bearings for a minimum period of 500 hrs. at  $600^\circ\text{F}$  and speeds between 20,000 and 45,000 rpm. None of the greases prepared and tested met this requirement. The unavailability of fluids sufficiently stable to provide the life required is primarily responsible. Several metal benzimidazoles and ferrocene derivatives were synthesized and tested as antigel agents for silicones. The former were ineffective. As additives for silicones, the ferrocene derivatives showed

excellent gel inhibition at high temperatures. Unfortunately, thickeners appear to negate this effect since no improvement in bearing performance life of greases containing them was realized. Approximately 100 materials were synthesized and/or purchased and tested as potential thickeners.

581. Hughes Aircraft Company, Culver City, California, NEW AND IMPROVED HEAT TRANSFER FLUIDS, REPORT FOR 15 FEBRUARY 1963 - 14 JANUARY 1964 by C. W. Mell and K. E. Hostetler, February 1964, Report No. TDR64 24A, AD-456 002, Contract No. AF33 657 8775 (Unclassified Report).

Study on extreme temperature range dielectric fluid coolants is described in detail. Experimental data are presented in a series of tables and graphs. Twenty-three new organic fluids composed of various silicone types, polyphenyl ethers, a ferrocene, a fluorocompound, and some of undetermined composition were studied. New candidate fluids are fully identified as to suppliers and their designations. In order to make electrical measurements at temperatures up to 650°F, an instrument was designed and a working model fabricated for static measurements of resistivity, dielectric constant, and dissipation-factor. Data were taken on several fluids from 77° to 650°F. An instrument was designed, a model fabricated, and data taken from static electric strength at temperatures from 77° to 650°F. Another instrument was designed, fabricated, and installed in the dynamic loop for determining the dynamic electric strength of fluids at temperatures to or above 650°F. The siloxane fluids appear to be the most promising for overall use, but the polyphenyl ethers show valuable high temperature stability. Fluids with lubricating properties have been found to be of concern to designers of electronic cooling systems.

582. Kalle, A., HEAT-FIXABLE LIGHT-SENSITIVE FERROCENE LAYERS, Netherlands Patent 6,504,126 (Cl. G 03c), Applied 18 October 1965, German patent applied 15 April 1964, 8 pp.

Mixtures of ferrocene and halogenated hydrocarbons ( $\text{CBr}_4$ ) are known to react under the influence of  $\gamma$ -radiation to form ferrocinium tetrahalogen ferrates. Such mixtures can also be used to form brown negative prints upon exposure to ultraviolet radiation or visible light, and these can be fixed by heating

at 80° to 120°, which causes evaporation of the unreacted components. The light-sensitivity of the systems is improved in the presence of amines or phenols which form dyes when exposed with CBr<sub>4</sub>. Substituted ferrocenes, e. g. diacetyl-ferrocene, can also be used, and synthetic resins or waxes to improve adhesion of the coatings to smooth-surfaced supports. In an example, paper is impregnated with a solution containing three g. each of ferrocene and CBr<sub>4</sub> and 0.1 g. 1-naphthylamine dissolved in a mixture of 15 cc. each of Me<sub>2</sub>CO and trichloroethylene, exposed, after drying, for 15 sec. through a transparency to a 200-w. W lamp, and passed by an infrared source, yielding a brown-violet copy.

583. Olin Mathieson Chemical Corporation, Chemicals Division, New Haven, Connecticut, SIB POLYMER DEVELOPMENT, QUARTERLY REPORT NO. 2, 1 MAY-31 JULY 1965 by H. A. Schroeder, August 1965, Report No. NOBS92143, AD-468 257 (Unclassified Report).

Our efforts dealt with "plain" SIB-2 and different variations of "modified" SIB-2; in addition, the newly discovered "off-ratio" SIB-2 was included in our program. Emphasis was placed on the study of parameters relevant to strength improvement such as the proper selection and concentration of reinforcing fillers and curing agents. The use of antioxidants was further stressed by the employment of a different grade of ferric oxide as well as an evaluation of ferrocene. A tensile strength retention between 35 to 50 percent at 600°F and up to 20 percent at 800°F was achieved. For the first time, the effects of heat-aging in air were investigated. The introduction of a minute number of chloromethyl groups into SIB-2 drastically improved solvent resistance. Off-ratio SIB-2, obtained by varying slightly the proportions of reactants during the polymer preparation, produces a cured elastomer with a tensile strength above 1000 psi. An investigation of the properties of SIB-4 was initiated. In this record, considerable improvement was made in preparing the first intermediate in the three-step polymer process. Cured test specimens showed a relatively low tensile strength at ambient temperature but an unusually high retention at 600°F.

584. Rai, C.,  
DERIVATIVES OF FERROCENE, U.S. Patent 3,222,373  
(cl. 260-299), 7 December 1965, Applied 6 June 1963, 3 pp.

The title compounds which have utility as scintillating agents and ultraviolet light absorbers were prepared by acylating ferrocene (I) with alkyl or aryl anhydride to form the oxo acid, reducing the latter to the corresponding mono- or dicarboxylic acid, and condensing the acid with an o-hydroxy, o-mercapto, or o-aminoaryl amine in the presence of polyphosphoric acid (II) catalyst. Thus,  $\text{CH}_2\text{Cl}_2$  (200 cc.) and 11.6 g.  $\text{AlCl}_3$  was added slowly to 9.29 g. I and 11 g. succinic anhydride, the mixture was stirred 2 hrs. and poured into ice to yield 4 g.  $\beta$ -ferrocenoylpropionic acid (III), m.  $168^\circ$ . III was hydrogenated in 250 cc. AcOH over 950 mg. Pt oxide under 30 psig. H for 48 hrs. and worked up in the conventional manner to yield 3.45 g.  $\gamma$ -ferrocenylbutyric acid (IV), m.  $116^\circ$ . IV (2.72 g.) and 1.5 g. o-aminothiophenol were added slowly to 50 g. II which was heated to  $100^\circ$ . The mixture was heated and stirred 2 hrs., cooled, and poured into ice, to precipitate 2.5 g. 1-(2-benzothiazolyl)-propylferrocene, m.  $108^\circ$ . A number of similar I derivatives are listed.

585. Resin Research Laboratories, Incorporated, Newark, New Jersey,  
HEAT STABLE INHIBITORS FOR DIENE VULCANIZATES by  
G. A. Baum and A. Goldberg, AD-268 271 (Unclassified Report).

Work was conducted to synthesize chemicals to function as heat resistant inhibitors for diene vulcanizates. Previous work revealed that a mixture of Ba and Cd salts of fatty acids combined with pentarythritol when added to diene rubber significantly reduced (about 50 percent) the damage caused by air over aging of the vulcanizate for 70 hrs. at  $300^\circ\text{F}$ . Substituted ferrocene derivatives, substituted resorcinol - formaldehyde derivatives, and polymeric secondary aryl amines were synthesized. Addition of these materials to styrene-butadiene rubber followed by vulcanization and heat aging showed that the resulting ferrocene derivatives were inactive as heat stabilizers, the resorcinol-formaldehyde resins adversely affected the curing of vulcanizates and functioned as oxidation promoters. The polymeric secondary aryl amines were relatively inactive, however the polyamine from p-phenylene diamine and p-dichlorobenzene showed

inhibition of degradation both alone and when mixed with a fatty acids soap/chelator combination. New classes of compounds which might function as heat stabilizers are being synthesized.

586. Resin Research Laboratories, Incorporated, Newark, New Jersey,  
HEAT STABLE INHIBITORS FOR DIENE VULCANIZATES  
by G. A. Baum and A. Goldberg, 1 November 1962, Report No. 1, Contract No. DA-11-070-508-ORD-1200 (Unclassified Report).

The objective of this work was to synthesize chemicals which would function as heat resistant inhibitors to diene vulcanizates, thus improving the heat resistance of "conventional" rubbers to a point where they may be considered for ordnance applications at temperatures above 212°F.

Previous work at Rock Island Arsenal has revealed that a mixture of barium and cadmium salts of fatty acids combined with pentaerythritol when added to diene rubber significantly reduced (about 50 percent) the damage caused by air oven aging of the vulcanizate for 70 hours at 300°F. It was hoped that other inhibitors could be synthesized which would yield the same degree of protection at 400°F. Current theories of thermal oxidative degradation of diene polymers agree that breakdown is initiated at the weakest carbon-carbon bonds, i. e., those in the beta position to the unsaturated linkage. Free radical units are thus produced which eventually lead to brittle crosslinked polymers of little utility.

Three distinct chemical classes of materials were synthesized during the past year. These included (1) substituted ferrocene derivatives which would stabilize free radicals as they were formed at elevated temperatures. This is because the ferrocene molecule easily gives up an electron to form the ferricinium ion; (2) substituted resorcinol-formaldehyde derivatives which would not only stabilize the elastomer through the reaction with free radicals, but which might possibly react with the residual olefinic linkages in the cured vulcanizate, and (3) polymeric secondary amines, which because of their lowered volatility at elevated temperatures as compared to the conventional diarylamine stabilizers, would continue to be effective free radical absorbers at 300°F and higher aging temperatures. Details describing the synthesis of 36 candidates are included in the report.



Addition of these materials to SBR (styrene-butadiene rubber) followed by vulcanization and heat aging, all compounding, curing and testing being performed by Rock Island Arsenal, showed the following results: the ferrocene derivatives were inactive as heat stabilizers, the resorcinol-formaldehyde resins adversely affected the curing of vulcanizates and in addition functioned as oxidation promoters rather than inhibitors. The polymeric secondary aryl amines were relatively inactive, however the polyamine from p-phenylene diamine and p-dichlorobenzene showed inhibition of degradation both alone and when mixed with a fatty acids soap/chelator combination.

587. Royal Aircraft Establishment, Farnborough, England,  
FERROCENE POLYMERS, II. THE POTENTIALITIES OF 1,1'-  
DIMETALOFERROCENES FOR THE SYNTHESIS OF HIGH-  
TEMPERATURE RESISTANT POLYMERS by W. A. Lee and  
B. So, AD-287 572, U.D.C. No. 678.767.25:536.495  
(Unclassified Report).

This review covers the potentialities of ferrocene compounds as precursors to high-temperature resistant polymers and the feasibility of using metaloferrocenes in their synthesis are discussed. Methods of preparation and reactions of metals ferrocenes are reviewed and suggestions for further work on their synthesis are made. Preliminary reactions to establish the feasibility of polymerization reactions are recommended. Sixty-six references are covered.

588. Sperry Gyroscope Company, Great Neck, New York,  
NUCLEAR RADIATION RESISTANT GYROSCOPE BEARING  
LUBRICANTS AND FLOTATION MEDIA by F. R. Callihan and  
R. A. Falk, Report No. TR60 753 P2, AD-274 844, Contract  
No. AF33 616 6817 (Unclassified Report).

Fluids for use as base stocks for the formulation of radiation-resistant lubricants were investigated; one of them, tert-butyl-1, 9-diphenylnonane, appears particularly promising and is recommended for further evaluation. Towards the objective of developing perfluoroaromatic materials, as highly stable fluids, methods for the preparation of hexafluorobenzene were investigated. A successful procedure involving the pyrolysis of dichlorofluoromethane was developed and is reported herein.

589. Wyandotte Chemicals Corporation, Michigan,  
SYNTHESIS AND EVALUATION OF HIGH TEMPERATURE  
STABLE AND NUCLEAR RADIATION STABLE METAL-  
CYCLOPENTADIENYL FLUIDS by R. L. Schaaf, P. T. Kan,  
and K. L. Rinehart, Jr., May 1960, Report No. TR58 187,  
AD-243 566, Contract No. AF33 616 5053 (Unclassified Report).

Not abstracted.

590. Wyandotte Chemicals Corporation, Michigan,  
SYNTHESIS OF METAL-CYCLOPENTADIENYL DERIVATIVES  
FOR USE AS ULTRAVIOLET ABSORBERS by R. L. Schaaf  
and K. L. Rinehart, Jr., April 1962, Report No. TR61 108  
P2, Ad-283 843, Contract No. AF33 616 7214 (Unclassified  
Report).

In a program toward synthesis of metal cyclopentadienyl compounds as additives, monomers, and polymers with high ultraviolet radiation resistance, 13 candidate ferrocenes were prepared, and the spectral characteristics in the 2000 to 5000 angstrom region were obtained. Additives prepared were 1,1'-bis(-flouorobenzoyl)-ferrocene, phenyl ferrocenoate, 1,1'-dibutylferrocene, 2-carboxybenzoylferrocene, benzoylferrocene oxime, 1,1'-bis(alpha-hydroxyethyl)-ferrocene, osmocene, and benzoylosmocene. Monomers synthesized were 1,1'-ferrocene diisocyanate, bis(2,3-epoxypropyl) 1,1'-ferrocenedicarboxylate, 1,1'-bis (n-methyl-n-(p-a inophenyl)-carboxamido)-ferrocene, dimethyl 1,1'-ferrocenedicarboxylate and 1,1'-di(hydroxymethyl)-ferrocene. 1,1'-diacetylferrocene reacted with benzene diazonium chloride to give 6-methyl-6-hydroxy-2-phenylazofulvene. Acetylation of acetamidoferrocene gave 1'-acetyl-1-acetamidoferrocene. The ratios of isomers formed in acetylation of mono- and di-bridged ferrocenes were measured accurately. 1,1'-diacetamidoferrocene, and a tri-bridge ferrocene were prepared.

591. Wyandotte Chemicals Corporation, Michigan,  
SYNTHESIS OF METAL-CYCLOPENTADIENYL DERIVATIVES  
FOR USE AS ULTRAVIOLET ABSORBERS, FINAL REPORT  
APRIL 1962 - JANUARY 1963 by K. L. Rinehart, Jr. and  
R. L. Schaaf, January 1963, Report No. WADD-TR-61-108,  
Pt. 111, X63-14269, Contract No. AF 33(616)-7214  
(Unclassified Report).

In a search for metallocene derivatives as additives,  
monomers, and polymers with high ultraviolet radiation

resistance, the preparation of osmocene and ruthenocene analogs of o-hydroxybenzophenone was investigated, and a study was made of the conversion of functional cyclopentadienes to ferrocenes. Isomeric bis- and tris-(trimethylene)ferrocenes were prepared and acetylated. The acetyl products were converted to the corresponding ferrocene-propionic acids, which on cyclization were shown to give homoannular ketonic products, as well as the expected heteroannular compounds.

#### D. Other Uses

592. Ethyl Corporation, Research Laboratories, Ferndale, Michigan, METAL-ORGANIC COMPOUNDS FOR VAPOR PLATING APPLICATION ANNUAL REPORT NO. 2, 1 MAY 1964-31 MAY 1965 by R. L. Mack, R. D. Stevenson, E. B. Rifkin, J. Kozikowski, and L. M. Niebylski, November 1965, Report No. TDR-64-206-PT-2, AD-476 821, Contract No. AF33(657)-11247, AF-7312 731201 (Unclassified Report).

This report covers progress in studies of the feasibility of vapor plating by depositing metals from selected metal-organics. The metals under study include AL, B, NB, HF, MO, SI, TA, and TI. Relatively pure deposits of AL and B were produced, as well as a pure codeposit of AL-TA. The most promising results to date are single deposits of MO and TI and codeposits of MO-SI and B-TI. Use of  $\text{NH}_3$  as an additive in the  $\text{H}_2$  carrier gas stream significantly reduced the decomposition temperature of dicyclopentadienyl hafnium dichloride. Future plans are to continue studies on the deposition of single metals, on codeposition from single metal-organics and from two metal-organics simultaneously, and on the use of  $\text{NH}_3$  and other reducing gases as carrier gases.

593. Ethyl Corporation, Research Laboratories, Ferndale, Michigan, METAL-ORGANIC COMPOUNDS FOR VAPOR-PLATING APPLICATIONS, QUARTERLY PROGRESS REPORT NO. 7, 1 JUNE - 31 AUGUST 1965 by R. L. Mack, R. D. Stevenson, and L. M. Niebylski, August 1965, Report No. GR-65-40, AD-467 741, Contract No. AF33 (657)-11247, AF-7312 731201 (Unclassified Report).

B plating runs using trimethylamine borane were made with the object of developing a technique for the precise control of vapor flow. Codeposits of B from trimethylamine borane and titanium from bis(-cyclopentadienyl) bis(pentafluorophenyl)

titanium or dicyclopentadienyl titanium dicarbonyl were studied. Unknown X-ray and electron diffraction patterns were obtained when the codeposits were analyzed. An acceptable, high-purity molybdenum deposit was obtained from mesitylene molybdenum tricarbonyl. A deposit made at a substrate temperature of 350°C contained more than 95 molecular percent molybdenum. Additional runs are planned to study the effect of system pressure, vapor-generator temperature, and carrier-gas composition on the coating.

594. Gill, T. J., III, and Mann, L. T., Jr.,  
SYNTHETIC POLYPEPTIDE ANTIGENS. XV. IMMUNOCHEMICAL PROPERTIES OF FERROCENYL-POLYGLU<sup>58</sup> LYS<sup>36</sup> TYR<sup>6</sup> (NO. 2) CONJUGATES, Journal of Immunology, Vol. 96, No. 5, 1966, pp. 906-912 (cf. CA 63, 15377g).

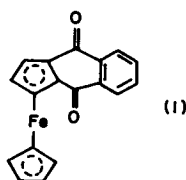
Ferrocenylmethyl isothiocyanate was conjugated with polyGlu<sup>58</sup> Lys<sup>36</sup> Tyr<sup>6</sup> to determine the number of ferrocenyl residues that can be conjugated with a macromolecule without exerting a significant hapten function and to determine how many ferrocenyl residues were necessary to act as antigenic determinants. Two ferrocenyl groups per polypeptide chain slightly enhanced the amount of antibody elicited, but only a small amount of the antibody was directed at the ferrocenyl group; ferrocene was useful as a label for metabolic studies at this level. Larger amounts of ferrocene (10 to 16 residues per polypeptide chain) showed strong hapten activity with  $\leq 70$  percent of the antibody directed at the ferrocenyl group; ferrocenyl acetic acid inhibited the ferrocene-antiferrocene reaction. The ability of ferrocene to enhance immunogenicity reflected behavior similar to that of aromatic amino acids and cyclohexylalanine. The metallocenes incorporate radioactive heavy metal atoms with relatively long half lives, are biologically stable and probably cannot be reutilized by the animal in any significant amount, and may become electron dense if short polymers of them are attached to the polypeptide chain. Nineteen references are included.

595. Lorkowski, H. J. and Wende, A.  
FERROCENE DERIVATIVES. IV. ACTIVATION OF PEROXIDE  
POLYMERIZATION OF UNSATURATED COMPOUNDS BY  
FERROCENE AND ITS SUBSTITUTION PRODUCTS, Plaste  
Kautschuk, Vol. 12, No. 9, 1965, pp. 527-528 (In German,  
cf. CA 62, 13178 g).

Addition of ferrocene to peroxide-initiated polymeriza-  
tions of unsaturated polyesters with styrene, copolymerization  
of polybutadiene with styrene, and of acrylonitrile causes  
increased activation. The catalysts used (for which time-  
temperature curves are plotted) are cyclohexanone peroxide,  
(BzO)<sub>2</sub> (with Co naphthenate), and ferrocene or its acetyl  
or hydroxymethyl derivatives.

596. Nesmeyanov, A. N., Vil'chevskays, V. D., Kochetkova, N. S.,  
and Gorelikova, Y. Y.,  
FERROCENEANTHRAQUIONE, USSR Patent 176,923 (Cl.  
C 07), 1 December 1965, Applied 19 March 1965 (Byul.  
Izobret. i Tovarnykh Znakov, No. 24, 1965, pp. 26-27).

The title compound (I) is prepared by treating ferrocene-  
anthrone with MnO<sub>2</sub> suspended in C<sub>6</sub>H<sub>6</sub>. A product suitable  
for dyeing wool, silk, and synthetic fibers is thus obtained.



597. Princeton University, Plastics Laboratory, Princeton,  
New Jersey,  
HIGH POLYMER RESEARCH by L. F. Rahm, AD-284 382  
(Unclassified Report).

Contents: Chemical Section: Polymerization of non-  
conjugated double bond systems, synthesis of multiple-strand  
polymers, ferrocene chemistry dielectrics section: semi-  
conduction in high polymers mechanical section: phase transi-  
tions in polypropylene, phase transitions in polybutene-1,  
deformation characteristics of spherulites, failure mechanism  
in glassy state polymers, flow behavior in polymer melts.

598. Texas Instruments Incorporated, Dallas, Texas,  
ORGANIC MATERIALS FOR ELECTRONIC APPLICATIONS,  
QUARTERLY PROGRESS REPORT NO. 2, 18 APRIL -  
17 JULY 1964 by R. E. Johnson and R. C. Sangster, July  
1964, Report No. TI-08064-112, AD-460 928, Contract No.  
AF33 615 1364 (Unclassified Report).

Organic polymer thin films have been prepared in the photoelectret configuration as the dielectric in a thin film field effect transistor. Because photomasking techniques using KMER attack the polymer, evaluation is not complete. The films by themselves do not induce a channel between the source and drain. No photoeffects are seen in the source-drain current if the organic film is illuminated. Preliminary investigations have been made to evaluate the organic polymer films as a capacitor dielectric and as a metal film insulator. Nickel squarate chelate polymers prepared at different temperatures have different polymer chain lengths and show different thermal activation energies of electrical conductivity. Chromium squarate polymer prepared in water solvent did not give measurable evaluation samples. Other solvents, such as dimethylformamide, are being evaluated for this polymer and for nickel squarate as well.

599. Wyandotte Chemicals Corporation, Michigan,  
INTERMEDIATES FOR HIGH TEMPERATURE STABLE  
POLYMERS, FINAL REPORT, 1 JANUARY-31 DECEMBER  
1964 by P. Szecsi, February 1965, Report No. TR-65-46,  
AD-464 487, Contract No. AF33 657 10819 (Unclassified  
Report).

The synthetic methods and experimental procedures adopted for the preparation of materials specified by RTD that are to be used as intermediates in high-temperature polymer studies are discussed. The compounds synthesized include ferrocenes, aromatic nitro and amino compounds, o-phenylenediamine derivatives, benzothiadiazole, a halotriazine, polyesters, and a number of polyfluoraromatic compounds.

600. Zehler, E. and Burke, C. L.,  
MEASUREMENTS OF TRUE DARK CONDUCTIVITIES IN  
FERROCENE CRYSTALS, Proceedings of the 1964 Army  
Science Conference, United States Military Academy, West  
Point, New York, 17-19 June 1964, Washington, D. C., Army  
Research Office, Office of the Chief, Research and Develop-  
ment, Vol. 2, 1964, p. 507, AD-611 869.

Systematic dark conductivity measurements on a monomeric organic crystal are described. The material chosen was ferrocene which, because of its relatively low room temperature resistivity of the order of  $10^{13}$  ohm cm and its simple structure, appears to be very suitable as a model substance for dark conductivity investigations. From the measurements performed, including voltage probing along the sample, long time observations, and measurement of resistivity with guard rings, it is established that the dark conductivity exists and cannot be explained as due to contact effects, dielectric relaxation, or surface conduction. Dependences of the conductivity on impurity content and crystal direction are difficult to determine and are discussed. Thermo-electric power data show that the Seebeck effect is as large as 1.2 mV/degree and that holes are more mobile than electrons.

## Section VII. REVIEW ARTICLES ON FERROCENE

601. Aerospace Technology Division, Library of Congress, Washington, D. C.,  
ORGANIC SEMICONDUCTORS, BIBLIOGRAPHY FOR 1960-1963, Author Unknown, July 1964, AD-455 166 (Unclassified Report).

This preliminary bibliography is based on Soviet open source materials available at the Aerospace Technology Division and the Library of Congress and covers five Soviet periodicals for the period 1960-1963. The periodicals, along with available translation journals, are listed. Library of Congress call numbers are provided for both original sources and the translation journals. These journals were selected for the preliminary report on the basis of frequency of reference to them in the major book found on the subject, *Organicheskiye Poluprovodniki* (Organic Semiconductors), Moscow, 1963, edited by the late Academician A. V. Topchiyev.

602. Author Unknown,  
METALLOCEDES, MONOGRAPH FROM ARAPAHOE  
CHEMICALS, INCORPORATED, BOULDER, COLORADO,  
January 1966.

Broad review covering ferrocene, nickelocene, cobaltocene, titanocenedichloride, zirconocene dichloride and O-hydroxybenzoyl ferrocene. The highlights of ferrocene chemistry are concisely covered in a well illustrated discussion covering 128 references on the ferrocene chemistry.

603. Birmingham, J. M.,  
CYCLOPENTADIENYL COMPOUNDS OF METALS, Chemical Engineering Progress, Vol. 58, No. 10, 1962, pp. 74-78.

A five page review covering 102 references which introduces the reader to the wide scope of knowledge, research, and uses available on cyclopentadienyl compounds of metals.



604. Birmingham, J. M.,  
SYNTHESIS OF CYCLOPENTADIENYL METAL COMPOUNDS,  
Advances in Organometallic Chemistry, New York, New York,  
Academic Press, 1964, Vol. 2.

This review, containing 425 references, covers the synthesis of cyclopentadienyl metal compounds by direct formation of cyclopentadienyl metal bonds from cyclopentadiene, the reaction of ionic cyclopentadienides with metal compounds, and reactions from alkenes and alkynes. It extensively covers synthesis by reactions of  $\pi$  bonded cyclopentadienyl metal compounds. An extensive tabular survey of synthesized compounds is given.

605. Coates, G. E.,  
ORGANO-METALLIC COMPOUNDS, London, England,  
Methuen and Company, Ltd. and New York, New York,  
John Wiley and Sons, Incorporated, 1960.

#### CONTENTS

##### Chapter

- I. The Alkali Metals
- II. Group II
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- VI. The Transition Elements  
Group VIII  
The Cyclopentadienyls

606. Coates, G. E.,  
ORGANO - METALLIC COMPOUNDS, London, England,  
Methuen and Company, Ltd., and New York, New York, John  
Wiley and Sons, Incorporated, Chapter VI.

In text book fashion the structure, bonding, synthesis, and electronic structure of ferrocene are covered. Only pre-1960 literature is referenced. The treatment is then expanded to other transition metal elements. Only a very brief mention of the organic reactions and synthesis in the ferrocene series are given.

607. Dyatkina, M. E.,  
(Title Not Available), Uspekhi Khimii, Vol. 27, 1958, pp.  
57-93 (In Russian).

A review, with 83 references through most of 1957, dealing with the electronic interpretation of metal complexes in structures related to ferrocene.

608. Ekemark, A. and Skaguis, K.,  
(Title Not Available), Acta Chemica Scandinavica, Vol. 16,  
1962, p. 1136.

Not abstracted.

609. Fischer, E. O.,  
METAL COMPOUNDS OF CYCLOPENTADIENE AND INDENE.  
Angewandte Chemie, Vol. 67, 1955, pp. 475-482.

A review, containing 80 references, covering the system of the metal dicyclopentadienyls (preparation, properties, combining ratios, and substituted compounds), metal diindenyls, and dicyclopentadienyl metal complexes.

610. Fischer, E. O. and Fritz, H. P.,  
COMPOUNDS OF AROMATIC RING SYSTEMS AND METALS,  
Advances in Inorganic Chemistry and Radio Chemistry, New  
York, New York, Academic Press, Incorporated, 1959, Vol.  
1, pp. 56-115.

This review covers 232 references up to 1958. The subjects are as follows:

## CONTENTS

- I. Introduction
- II. Complex Formation by Five-Membered Ring Systems
  - A. Dicyclopentadienyl Iron
  - B. Preparative Methods for Metal Cyclopentadienyls
  - C. Chemical Properties of Pure Cyclopentadienyl Metal Compounds
  - D. Physicochemical and Crystallographic Properties of Pure Metal Cyclopentadienyl Compounds
  - E. Ferrocene as an Organic Compound
  - F. Mixed Cyclopentadienyl Metal Complexes
  - G. Molecular Structure and Bonding

- H. Technical Applications of Cyclopentadienyl Metal Complexes
- III. Complex Formation by Six-Membered Ring Systems
  - A. Introduction
  - B. Preparative Methods
  - C. Complexes Containing Two Six-Membered Rings
  - D. Mixed Complexes Containing Six-Membered Rings
  - E. Physicochemical Investigations
  - F. Structure and Bonding
  - G. The Elucidation of the Constitution of the Chromium Phenyl Compounds
- IV. The Existence of Complexes of Seven-Membered Aromatic Systems

611. Fischer, E. O. and Werner, H.,  
METAL II COMPLEXES, Complexes with di-and Oligo-Olefinic Ligands, Amsterdam, Holland, London, England, New York, New York, Elsevier Publishing Company, 1966, Vol. 1.

The concept of metal  $\pi$ -complexes is often associated with the names of ferrocene and dibenzenechromium. Preparation of these two compounds was indeed the starting point of a development which has had a fruitful effect on both theoretical and preparative chemistry, and whose boundaries cannot as yet be envisaged. In addition to aromatic systems such as the cyclopentadienyl anion, the tropylium cation and benzene, a large number of straightchain and cyclic olefins, with varying numbers of double bonds, have recently been used as ligands in metal  $\pi$ -complexes. The growth of the literature in this field has made advisable a subdivision into, mono-olefins on the one hand and into di- and oligo-olefins on the other. The present survey deals exclusively with the latter group of compounds.

## CONTENTS

- I. Introduction
- II. Historical
- III. Bonding theories
- IV. General methods of preparation
- V. General discussion of preparative results
- VI. Metal complexes with  $\pi$ -allylic ligands

612. Foreign Technology Division, Wright-Patterson Air Force Base, Ohio,  
ORGANOSILICON DERIVATIVES OF DICYCLOPENTADIENYL IRON by G. Wu, July 1965, Report No. TT 65-62630, AD-618 007, FTD-TT-64-1345, (Unclassified Report).

Not abstracted.

613. Fritz, H. P.,  
INFRARED AND RAMAN SPECTRAL STUDIES OF  $\pi$  COMPLEXES FORMED BETWEEN METALS AND  $C_NH_N$  RINGS, Advances in Organometallic Chemistry, Vol. 1, New York, New York, Academic Press, 1964, pp. 239-316.

This review covers 158 references. The coverage is very broad covering other metals than iron and monoring metal compounds as well as various ring systems besides cyclopentadiene.

## CONTENTS

- I. Introduction
- II. Theoretical Considerations in the Analysis of Vibrational Spectra
  - A. Principles of Molecular Spectroscopy
  - B. Interpretation of Observed Spectra
- III. Techniques of Infrared and Raman Spectroscopy
  - A. Spectrophotometers
  - B. Preparation of Samples
- IV. General Aspects of the Analysis of Spectra of  $\pi$  Complexes of Cyclic Systems,  $C_NH_N$ 
  - A. Cyclic Hydrocarbons
  - B.  $\pi$  Complexes
- V. Experimental Results for Three-Membered Rings
- VI. Experimental Results for Four-Membered Rings
  - A. General Remarks
  - B. Special Cases
- VII. Experimental Results for Five-Membered Rings
  - A. Cyclopentadienyl Anion,  $(C_5H_5)^-$
  - B. Metal Cyclopentadienyls
- VIII. Experimental Results for Six-Membered Rings
  - A. Benzene
  - B. Benzene-Metal Complexes
- IX. Experimental Results for Seven-Membered Rings
  - A. Tropylium Cation,  $(C_7H_7)^+$
  - B.  $\pi$ - $C_7H_7$ -Metal Complexes

- X. Experimental Results for Eight-Membered Rings
  - A. Cyclooctatetraenyl Anion,  $(C_8H_8)^{2-}$
  - B.  $\pi-C_8H_8$ -Metal Complexes
- XI. Some Quantities Derived from Vibrational Spectra
- References
- Supplementary References

614. King, R. B.,  
ORGANOMETALLIC SYNTHESSES, Transition-Metal Com-  
pounds, Vol. 1, New York, New York, and London, England,  
 Academic Press, 1965.

## CONTENTS

### Part I. General Techniques in Transition-Metal Organo- metallic Chemistry

- A. Techniques for Carrying Out Reactions
- B. Techniques for Isolating and Purifying Products
- C. Techniques for Identifying Products
- D. Precautions

### Part II. Preparations of Specific Transition-Metal Organo- metallic Compounds

- A. Biscyclopentadienylmetal Derivatives
- B. Metal Carbonyls Without Other Ligands
- C. Cyclopentadienylmetal Carbonyls
- D. Olefins and Acetylene Metal Complexes
- E. Arene Metal Complexes
- F. Cycloheptatrienyl and Cycloheptadienyl Metal Complexes
- G. Alkyl, Acyl, and Perfluoroalkyl Metal Carbonyls
- H. Metal Carbonyl Hydride Derivatives
  - I. Metal Nitrosyl Derivatives
  - J. Metal Carbonyl Halide Derivatives
- K. Metal Carbonyl Derivatives with Phosphorus

Laboratory techniques in this field, giving specific procedures for synthesis in the tradition of "Organic Synthesis," are presented in a 181 page book.

615. King, R. B. and Stone, F. G. A.,  
(Title Not Available), Inorganic Synthesis, Vol. 7, 1963,  
p. 99.

Not abstracted.

616. Little, W. F.,  
METALLOCENES, Survey of Progress in Chemistry, Vol. 1,  
New York, New York, Academic Press, 1963.

A well rounded coverage of the entire chemistry of metallocenes up to 1962. The discovery and structure of ferrocene is discussed followed by the preparative methods used to synthesize ferrocene and its homologs. Next the reactions of ferrocene are reviewed and the electronic effects in the ferrocene series are covered. Discussions of bridged ferrocenes, polymers containing ferrocene, and structural determination follow.

The other metallocenes are then reviewed by dividing them into three classes: Ionic compounds, sigma bonded compounds, and  $\pi$  cyclopentadienyl compounds. Two hundred and forty five references are covered.

617. Nesmeyanov, A. N.,  
SUBSTITUTION IN THE FERROCENE NUCLEUS, Proceedings of the Royal Society, Vol. 246, 1958, pp. 495-503.

This is a published lecture by A. N. Nesmeyanov delivered to the Royal Society on 24 November 1955. It covers the general aspects of substitution in the ferrocene nucleus drawing on 17 references plus numerous examples from Nesmeyanov's own laboratory. The aromatic nature combined with the ease of oxidation are major factors in the reaction paths available to ferrocene.

618. Nesmeyanov, A. N. and Perevalova, E. G.,  
CYCLOPENTADIENYL COMPOUNDS OF METALS AND RELATED COMPOUNDS, Uspekhi Khimii, Vol. 27, 1958, pp. 3-56.

A selective review in English written by the most productive chemist in the metallocene field. It covers methods of preparing metallocene compounds, physical and chemical properties of ferrocenes, lists chemical reactions by types such as oxidation, acylation, alkylation, etc., dicyclopentadienyl

compounds of elements of groups VIII, VII, VI, V, IV, III, II, and I of the periodic table, cyclopentadienyl carbonyl and nitrocyl metal compounds and diindenyl and dibenzene type organometalics, orderly tables, hundreds of compounds, their method of preparation, yield, and literature references. Most valuable to the chemist is the coverage of the Russian and German literature. Two hundred and nineteen references are covered.

619. Nesmeyanov, A. N. and Perevalova, E. G.,  
RECENT ADVANCES IN FERROCENE CHEMISTRY IN THE  
USSR, Ann. N. Y. Acad. Sci., Vol. 125, No. 1, 1965, pp.  
67-88.

A review with 132 references.

620. Nesmeyanov, A. N., Romanenko, V. I., and Sazonova, V. A.,  
BASICITY CONSTANTS OF AMINES DERIVED FROM FERRO-  
CENE, Izvestiya Akademii Nauk SSSR, Seriya Khimii, Vol. 375,  
1966.

Not abstracted

621. Pauson, P. L.,  
FERROCENE AND RELATED COMPOUNDS, Quarterly  
Reviews, Vol. 9, 1955, pp. 391-414.

This is the earliest of the ferrocene reviews and covers the literature (88 references) concerning the structure, bonding theoretical treatment, preparation, properties and reactions of ferrocenes, and ferrocene derivatives through 1955.

622. Pauson, P. L.,  
ORGANOMETALLIC CHEMISTRY, New York, New York,  
Reinhold Publishing Corporation, 1960, pp. 346-379, ACS  
Monograph No. 147.

This review largely concentrates on ferrocene and covers well the pre- 1960 literature. Preparation, properties, structure, aromatic substitution reactions (such as Friedel-Crafts acylation, sulfonation, mercuration, arylation, condensations, metalation), and reactions of iron are covered in a concise manner.

623. Plesske, K.,  
RING SUBSTITUTIONS AND SECONDARY REACTIONS OF  
AROMATIC - METAL - II COMPLEXES, PART II., Angewante  
Chemie (International Edition), Part II, Vol. 1, 1962, pp. 394-  
399, and Part I, Vol. 1, 1962, p. 312.

A review with 140 references. This review is heavily oriented to the synthesis, reactions, and generally the organic chemistry of ferrocene and its derivatives. It covers well the German and Russian literature and is especially valuable since the review is in English.

624. Rausch, M. D.,  
METALLOCENE CHEMISTRY - A DECADE OF PROGRESS,  
Canadian Journal of Chemistry, Vol. 41, 1963 (Presented  
at the Symposium on Organometallic Compounds, Vancouver,  
British Columbia, 4-6 September 1962).

One of the most significant new frontiers in chemistry during the past decade has been the stabilization and study of  $\pi$ -organic derivatives of the transition metals. Over 60 elements are now known to form one or more cyclopentadienyl compounds. The aromatic-type reactions displayed by ferrocene and related complexes have also been extensively investigated. Ferrocene will undergo alkylation, acylation, sulphonation, metalation, arylation, formylation, aminomethylation, and other reactions characteristic of a highly reactive aromatic system.  $\pi$ -Cyclopentadienyl derivatives of vanadium, chromium, manganese, ruthenium, and osmium as well as certain  $\pi$ -arene complexes of chromium exhibit ring substitution reactions in varying degrees. Other metallocenes undergo ring addition reactions.

The orientation effects of substituents on reactions of substituted ferrocenes have been studied. A variety of unique oxidation, reduction, dehydration, and rearrangement reactions are known in metallocene chemistry. Haloferrocenes and mercuriferrocenes are readily converted to biferrocenyl. Recent rate investigations have established that carbonium ions adjacent to metallocene nuclei possess unusual stabilization as a result of direct metal participation.



625. Rausch, M., Vogel, M. and Rosenberg, H.,  
FERROCENE, A NOVEL ORGANOMETALLIC COMPOUND,  
Journal Chemical Education, Vol. 34, 1957, pp. 268-272.

A brief review of some of the important aspects concerning preparation, physical properties, structure, aromatic character, reactions, and applications of ferrocene. It covers 51 references up to 1956. The coverage is in simple, elementary language. A good introduction to ferrocene for those who are not engaged in research in this area.

626. Royal Aircraft Establishment, Farnborough, England,  
FERROCENE POLYMERS, PART I. A LITERATURE REVIEW  
by W. A. Lee, AD-269 708 (Unclassified Report).

The preparation and properties of addition, condensation, and recombination polymers of ferrocene are reviewed. There is a general lack of information about most of these systems. Uses have been claimed for some polymers as lubricants, adhesives, rubbers, and plastics. The magnetic properties of some of these polymers are discussed. Forty-nine references are included.

627. Royal Aircraft Establishment, Farnborough, England,  
FERROCENE POLYMERS II. THE POTENTIALITIES OF  
1,1'-DIMETALLO FERROCENES FOR THE SYNTHESIS OF  
HIGH-TEMPERATURE RESISTANT POLYMERS by W. A.  
Lee and B. So, AD-287,572, U. D. C. No. 678.767.25:536.495.

This review covers the potentialities of ferrocene compounds as precursors to high-temperature resistant polymers and the feasibility of using metallocenes in their synthesis are discussed. Methods of preparation and reactions of metallocenes are reviewed and suggestions for further work on their synthesis are made. Preliminary reactions to establish the feasibility of polymerization reactions are recommended. Sixty-six references are covered.

628. Schlogel, K.,  
FERROCENE AND RELATED METAL CYCLOPENTADIENYLS,  
Osterr. Chemiker-Ztg., Vol. 59, 1958, pp. 93-104.

Although not held we should include the reference because  
of Schlogel's important contributions to the field

629. Swaminathan and Ranganathan,  
FERROCENE AND RELATED COMPOUNDS, Current Science  
(India), Vol. 25, 1958, pp. 6-8.

Not abstracted.

630. Wardlaw and Bradley,  
ORGANIC COMPOUNDS OF METALS, Endeavor, Vol. 14,  
1955, pp. 140-145.

Not abstracted.

631. Wilkinson, G. and Cotton, F. A.,  
CYCLOPENTADIENYL AND ARENE METAL COMPOUNDS,  
Progress in Inorganic Chemistry, New York, New York,  
Interscience Publishers, Vol. 1, 1959, pp. 1-124.

This is an extremely comprehensive review of  
cyclopentadienyl and arene metal compounds. It covers the  
chemistry of compounds formed between transition metals and  
the cyclopentadienyl group, benzene and related systems, and  
unsaturated hydrocarbons. It deals also with ionic derivatives  
of the cyclopentadiene ion. Comprehensive coverage of the  
literature to 1958 is found.

## CONTENTS

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- D. Some Chemical Properties
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  - B. Cycloheptatriene and Azulene Metal Complexes
  - C. Quinone and Tetracyclone Metal Complexes
  - D. Other Possible Systems
- References

632. Wu, K.,  
 ORGANOSILICON DERIVATIVES OF FERROCENE, Hua Hsueh T'ung Pao, Vol. 5, 1963, pp. 293-301, AD-618 007.

A review of the synthetic methods for the title compounds, especially for the different types of ferrocene-siloxanes. Twenty-one references are given.

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